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(54) Title: RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

(57) Abstract: A radiation-curable composition that includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component, and a photoinitiator component is provided.

RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to radiation-curable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component.

Brief Description of Related Technology

Cyanoacrylates generally are quick setting materials which cure to clear, hard glassy resins, useful as sealants, coatings, and particularly adhesives for bonding together a variety of substrates [see e.g., H.V. Coover, D.W. Dreifus and J.T. O'Connor, "Cyanoacrylate Adhesives" in Handbook of Adhesives, 27, 463-77, I. Skeist, ed., Van Nostrand Reinhold, New York, 3rd ed. (1990)].

Ordinarily, upon contact with substrate materials possessing a surface nucleophile, cyanoacrylate-containing compositions spontaneously polymerize to form a cured material. The cured material exhibits excellent adhesive properties to materials such as metals, plastics, elastomers, fabrics, woods, ceramics and the like.

Cyanoacrylate-containing compositions are thus seen as a versatile class of single-component, ambient temperature curing adhesives.

With conventional polymerizable compositions other than those containing cyanoacrylate monomers, radiation cure generally presents certain advantages over other known cure methods. Those advantages include reduced cure time, solvent elimination (which thereby reduces environmental pollution, and conserves raw materials and energy) and inducement of low thermal stressing of substrate material. Also, room temperature radiation cure prevents degradation of certain heat sensitive polymers, which may occur during a thermal cure procedure.

Radiation-curable, resin-based compositions are legion for a variety of uses in diverse industries, such as coatings, printing, electronic, medical and general engineering. Commonly, radiation-curable compositions are used for adhesives, and certain of the compositions are acrylate-based compositions.

Well-known examples of radiation-curable, acrylate-based resins include those having structural backbones of urethanes, amides, imides, ethers, hydrocarbons, esters and siloxanes. [See e.g., J.G. Woods, "Radiation-Curable Adhesives" in Radiation Curing: Science and Technology, 333-98, 371, S.P. Pappas, ed., Plenum Press, New York (1992).] The common cure mechanism for such radiation-curable, acrylate-based compositions is reported to be free-radical polymerization.

European Patent Publication EP 393 407 describes a radiation-curable composition which includes a slow cure cationic polymerizable epoxide, a fast cure free radical polymerizable acrylic component and a photoinitiator. Upon exposure to radiation, the photoinitiator is said to be capable of generating a cationic species which is capable of initiating polymerization of the epoxide and a free radical species which is capable of initiating polymerization of the acrylic component. The polymerizable acrylic component

includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters, examples of which are expressed as 2-cyanoethyl acrylate ($CH_2=CHCOOCH_2CH_2CN$) and 3-cyanopropyl acrylate ($CH_2=CHCOOCH_2CH_2CH_2CN$). (See page 5, lines 19-26.)

U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

In C. Kutal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^-, cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Kutal) 5,691,113 (Kutal) and 5,877,230 (Kutal).

International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α-cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VII of the periodic table and aromatic electron system ligands selected from π-arenes, indenyl, and η-cyclopentadienyl. The photocurable composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni)

describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition component would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism, thereby providing to the compositions (and cured reaction products formed therefrom) the benefits and advantages of curing through such a mechanism. More specifically, photocurable compositions of this invention cure rapidly when used, and in so doing minimize the opportunity for undesirable blooming or crazing formation in the cured reaction product. In addition, the inventive photocurable compositions are capable of curing through larger gaps between substrate surfaces than conventional cyanoacrylates, or known photocurable cyanoacrylates. Moreover, as set forth in greater detail below, in one aspect of the invention the photocurable compositions include a non-cyanoacrylate-based radical curable component. The precense of such a component in the inventive compositions allows for the generation of copolymers and reaction products, which would not otherwise be accesible through typical anionic polymerization mechsanisms -- the predominant polymerization of cyanoacrylates.

In another aspect of the present invention, there is provided a method of polymerizing a photocurable composition by providing an amount of the composition to a desired surface and exposing the composition to radiation in an amount sufficient to effect cure thereof.

In yet another aspect of the present invention, there is provided the cured reaction product formed from a photocurable composition after exposure thereof to a curingly effective amount of radiation.

The present invention will be more readily appreciated by those persons of skill in the art based on a reading of the detailed description of the invention which follows and the examples presented thereafter for illustrative purposes.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to photocurable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoiniated radical generating component and a photoinitiator component.

The cyanoacrylate component or cyanoacrylate-containing formulation includes cyanoacrylate monomers which may be chosen with a raft of substituents, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, such as n-propyl- or i-propyl-2-cyanoacrylate, butyl-2-cyanoacrylates, such as n-butyl- or i-butyl-2-cyanoacyrlate, octyl-2-cyanoacrylates, such as n-alkyl-, 2-alkyl-2-cyanoacrylate, and the like, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable cyanoacrylate monomer for use herein is ethyl-2-cyanoacrylate.

Among the different types of materials appropriate for use as the photoiniated radical generating component desirable ones share at least these common features: they possess electron withdrawing substituents present at at least one portion of the molecule, thereby rendering the portion(s) electron deficient. And when placed in contact with a photoexcitable material (such as a dye), which when exposed to radiation of an appropriate wavelength, absorbs energy sufficient to cause the radical initiator to cleave at the electron deficient portion(s) of the molecule, thereby generating free radicals.

A variety of photoiniated radical generating components are suitable for use herein, such as α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, and peresters. Of course, combinations of these compounds may also be used.

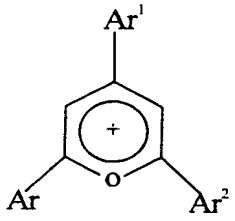
More specific examples of such materials include azoisobutyronitrile ("AIBN"), 1,1'-azo-bis(cyclohexane carbonitrile) ("ABCH"), 4,4'-azo-bis(4-cyanovaleric acid) ("ABCV"), 1,1'-(azodicarbonyl)-dipiperidine ("ADCDP"), 1,1-bis(t-butylperoxy)cyclohexane ("BBPH"), 2,5-bis(t-butylperoxy)2,5-dimethylhexane ("BBPDMH"), bis[1-(t-butylperoxy)-1-methyl-ethyl]benzene ("BBPMEB"), benzoin methylether ("BME"), cumylhydroperoxide ("CHPO"), dibenzoylperoxide ("DBPO"), di-t-butylperoxide ("DTBPO"), 2,2-diethoxyacetophenone ("DEAP"), 2,2-dimethoxy-phenylacetophenone ("DMPAP"), dicumylperoxide ("DCPO"), diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide ("DPTPO"), desylchloride ("DC"), lauroylperoxide ("LPO"), t-butylperoxybenzoate ("TBPB"), and t-butylhydroperoxide ("TBHPO").

Other examples include those available commercially from Ciba Specialty Chemicals Corp., Tarrytown, New York under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl) phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one), and 819 [bis(2,4,6-trimethyl benzoyl) phenyl phosphine oxide] and "DAROCUR" 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and 4265 (the combination of 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one); and the visible light [blue] photoinitiators, dl-camphorquinone and "IRGACURE" 784DC (bis(η^5-2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium).

Of course, combinations of these materials may also be employed herein.

Photoinitiators enhance the rapidity of the curing process when the radiation compositions are exposed to electromagnetic radiation. A number of photoinitiators may be employed herein, examples of which include, but are not limited to,

Photoinitiators useful herein include pyrylium-based materials having a core structure of



X^-

where each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion, such as halogen, hexahalophosphate, hexahaloarsenate, hexahaloantimonate, tetrahaloferrate, tetrahaloborate (e.g., fluoro, chloro, bromo and iodo), and sulfonate.

More specific representations of the pyrylium-based materials include: 2,4,6-triphenylpyrylium-tetrafluoroborate ("TPT"), 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium-tetrafluoroborate) ("PBT"), 2,4-diphenylnaphto-(1,2-B) pyrylium-tetrafluoroborate ("DNT"), 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate ("TPTS"), and 2,6-dipenyl-4(p-tolyl)-pyrylium tetrafluoroborate ("DTPT").

In the aspect of the invention where a non-cyanoacrylate-based radical curable component is included in the inventive compositions, such radical curable component may be selected from a wide variety of materials, such as alkenes or alkynes.

Of these, styrene and derivatives thereof, such as alkyl- and alkenyl-ether derivatives, (meth)acrylates, alkyl- and aryl or alkenyl acetylenes, as well as esters of vinyl alcohol (e.g., vinyl acetate), are particularly desirable.

With respect to formulating photocurable compositions, generally the components may be introduced to one another in any convenient order. Alternatively, it may be desirable to prepare a premix of the radical initiator component and the photoinitiator component. In this way, a ready made premix of those components may be added to the cyanoacrylate component of the formulation to allow for a quick and easy one-part formulation of a photocurable composition prior to dispensing and curing thereof.

For packaging and dispensing purposes, it may be desirable for photocurable compositions in accordance with the present invention to be relatively fluid and flowable. Variations in the viscosity thereof may also be desirable in certain applications and may be readily achieved through routine changes in formulation, the precise changes being left to those persons of ordinary skill in the art.

For instance, ordinarily cyanoacrylate-containing compositions free from an added thickener or viscosity modifier are low viscosity formulations (such as in the range of 1 to 3 cps). While a composition with such a viscosity (or one whose viscosity has been modified to be up to about five times that viscosity) may be appropriate for a wicking application where a small gap exists between sustrates to be bound (e.g., less than about 0.1 mils) and/or an application where enhanced cure speed is desirable, such a viscosity may be too low for convenient use in certain industrial applications. At least for this reason, the viscosity of cyanoacrylate-containing compositions has at times been desirably modified through, for instance, the addition of polymethylmethacrylates and/or fumed silicas. See e.g., U.S. Patent Nos. 4,533,422 (Litke) and Re. 32,889 (Litke), the disclosures of each of which are hereby expressly incorporated herein by reference.

A medium viscosity formulation (such as in the range of 100 to 300 cps) may be more appropriate in applications where greater control of flowability is desirable. And a high viscosity formulation (such as in the

range of 600 to 1000 cps) may be more appropriate in applications involving porous substrates and/or substrates with larger gaps (such as greater than about 0.5 mils).

Of course, those persons of skill in the art should make appropriate decisions regarding whether a viscosity modifier should be included in the photocurable composition, and if so which one(s) and at what level should one be included to achieve the desired viscosity for the intended applications.

In addition, it may be desirable to toughen the cured photocurable compositions of the present invention through the addition of elastomeric rubbers such as is taught by and claimed in U.S. Patent No. 4,440,910 (O'Connor), the disclosure of which is hereby expressly incorporated herein by reference. It may also be desirable to improve the hot strength of the cured photocurable compositions by addition of anhydrides, such as is taught by and claimed in U.S. Patent No. 4,450,265 (Harris) and the documents cited therein, the disclosures of each of which are hereby expressly incorporated herein by reference.

Moreover, the compositions of the present invention may be rendered into a thixotropic paste through addition of powdered organic fillers having a particle size of about 2 to 200 microns as is taught by U.S. Patent No. 4,105,715 (Gleave) or thickened by a copolymer or terpolymer resin to improve peel strength as is taught by U.S. Patent No. 4,102,945 (Gleave), the disclosures of each of which are hereby incorporated herein by reference.

Further, the compositions of the present invention may be rendered more resistant to thermal degradation at elevated temperature conditions by the inclusion of certain sulfur-containing compounds, such as sulfonates, sulfinates, sulfates, sultones and sulfites as set forth in U.S. Patent No. 5,328,944 (Attarwala), the disclosure of which is hereby expressly incorporated herein by reference. The inclusion of such compounds in the photocurable compositions of the present invention renders those compositions well-suited for

applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a phtotiniated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α-halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phospine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or

ketocoumarine derivatives, in an amount within the range of about 0.5% to about 10% by weight of the composition, with about 2% to about 4% or greater by weight of the total composition being desirable. The balance of the composition is composed predominantly of a cyanoacrylate component, such as ethyl-2-cyanoacrylate. Of course, the amount of all the components -- including stabilizers -- together in the composition totals 100%.

A method of curing a photocurable composition in accordance with this invention is also provided herein, the steps of which include (a) providing onto a desired surface an amount of a photocurable composition; and (b) subjecting the composition to radiation sufficient to effect cure thereof.

The amount of photocurable composition provided should be sufficient to cure and form an adequate bond to the substrate surfaces between which it is applied. For instance, application of the photocurable composition may be achieved by dispensing the composition in drop-wise fashion, or as a liquid stream, brush-applied, dipping, and the like, to form a thin film. Application of the photocurable composition may depend on the flowability or viscosity of the composition. To that end, viscosity modifiers, as noted above, may be included in the composition.

The photocurable compositions of the present invention have taken the ordinary undesirable by-product free radical reaction that compromises shelf life stability and turned it into a controlled free radical cure mechanism.

In use, such compositions are desirably readily dispensed onto a portion of a desired surface of a substrate onto which is to be bonded a portion of another substrate. The photocurable composition may be applied to certain portions of the substrate surface or over the entire surface of the substrate to be bonded, depending on the particular application.

The source of radiation emitting electromagnetic waves is selected from ultraviolet light, visible light,

electron beam, x-rays, infrared radiation and combinations thereof. Desirably, ultraviolet light is the radiation of choice, with appropriate sources including "H", "D", "V", "X", "M" and "A" lamps, mercury arc lamps, and xenon arc lamps (such as those commercially available from Loctite Corporation, Rocky Hill, Connecticut; Fusion UV Curing Systems, Buffalo Grove, Illinois; Spectroline, Westbury, New York; or Xenon Corp., Woburn, Massachusetts; microwave-generated ultraviolet radiation; solar power and fluorescent light sources. Any of these electromagnetic radiation sources may use in conjunction therewith reflectors and/or filters, so as to focus the emitted radiation onto a specific portion of a substrate onto which has been dispensed a photocurable composition and/or within a particular region of the electromagnetic spectrum. Similarly, the electromagnetic radiation may be generated directly in a steady fashion or in an intermittent fashion so as to minimize the degree of heat build-up. Although the electromagnetic radiation employed to cure the photocurable compositions into desired reaction products is often referred to herein as being in the ultraviolet region, that is not to say that radiation in other regions within the electromagnetic spectrum may not also be suitable. For instance, in certain situations, radiation in the visible region of the electromagnetic spectrum may also be advantageously employed, whether alone or in combination with, for instance, radiation in the ultraviolet region. Of course, microwave and infrared radiation may also be advantageously employed under appropriate conditions.

Higher or lower radiation intensities, greater or fewer exposures thereto and length of exposure and/or greater or lesser distances of the source of radiation to the composition may be required to complete curing, depending of course on the particular components of a chosen composition.

More specifically with respect to radiation intensity, the chosen lamp should have a power rating of at

least about 100 watts per inch (about 40 watts per cm), with a power rating of at least about 300 watts per inch (about 120 watts per cm) being particularly desirable. Also, since the inclusion of a photoinitiator in the composition may shift the wavelength within the electromagnetic radiation spectrum at which cure occurs, it may be desirable to use a source of electromagnetic radiation whose variables (e.g., wavelength, distance, and the like) are readily adjustable.

During the curing process, the composition will be exposed to a source of electromagnetic radiation that emits an amount of energy, measured in mW/cm^2, determined by parameters including: the size, type and geometry of the source; the duration of the exposure to electromagnetic radiation; the intensity of the radiation (and that portion of radiation emitted within the region appropriate to effect curing); the absorbency of electromagnetic radiation by any intervening materials, such as substrates; and the distance the composition lies from the source of radiation. Those persons of skill in the art should readily appreciate that curing of the composition may be optimized by choosing appropriate values for these parameters in view of the particular components of the composition.

To effect cure, the source of electromagnetic radiation may remain stationary while the composition passes through its path. Alternatively, a substrate coated with the photocurable composition may remain stationary while the source of electromagnetic radiation passes thereover or therearound to complete the transformation from composition to reaction product. Still alternatively, both may traverse one another, or for that matter remain stationary, provided that the photocurable composition is exposed to electromagnetic radiation sufficient to effect cure.

Commercially available curing systems, such as the "ZETA" 7200 or 7400 ultraviolet curing chamber (Loctite Corporation, Rocky Hill, Connecticut), "UVALOC" 1000 (Loctite Deutschland GmbH, Münich, Germany), Fusion UV Curing Systems F-300 B (Fusion UV Curing Systems, Buffalo

Grove, Illinois), Hanovia UV Curing System (Hanovia Corp., Newark, New Jersey), BlackLight Model B-100 (Spectroline, Westbury, New York), and RC500 A Pulsed UV Curing System (Xenon Corp., Woburn, Massachusetts), are well-suited for the purposes described herein. Also, a Sunlighter UV chamber fitted with low intensity mercury vapor lamps and a turntable may be employed herein.

The required amount of energy may be delivered by exposing the composition to a less powerful intensity of electromagnetic radiation for a longer period of time, through for example multiple passes, or alternatively, by exposing the composition to a more powerful intensity of electromagnetic radiation for a shorter period of time. In addition, each of those multiple passes may occur with an intensity at different energy intensities. In any event, those persons of skill in the art should choose an appropriate intensity of electromagnetic radiation depending on the particular composition, and position the source of electronic radiation at a suitable distance therefrom which, together with the length of exposure, optimizes transformation. Also, it may be desirable to use a source of electromagnetic radiation that is delivered in an intermittent fashion, such as by pulsing or strobing, so as to ensure a thorough and complete cure without causing excessive heat build-up.

In use, a photocurable composition in accordance with the present invention may be dispensed, such as in the form of a thin film or droplet, onto a desired substrate. Substrates onto which the photocurable composition of the present invention may be applied may be chosen from a vast selection of different materials; basically, any material with which cyanoacrylates may be used is suitable as well for use herein. See supra.

Desirable choices among such materials include acrylics, epoxies, polyolefins, polycarbonates, polysulfones (e.g., polyether sulfone), polyvinyl acetates, polyamides, polyetherimides, polyimides and derivatives and co-polymers

thereof with which may be blended or compounded traditional additives for aiding processibility or modifying the physical properties and characteristics of the material to be used as a substrate. Examples of co-polymers which may be employed as substrates include acrylonitrile-butadiene-styrene, styrene-acrylonitrile cellulose, aromatic copolyesters based on terephthallic acid, *p,p*-dihydroxybiphenyl and *p*-hydroxy benzoic acid, polyalkylene (such as polybutylene or polyethylene) terephthalate, polymethyl pentene, polyphenylene oxide or sulfide, polystyrene, polyurethane, polyvinylchloride, and the like. Of course, other materials may also be employed for use herein. Particularly, desirable co-polymers include those which are capable of transmitting UV and/or visible radiation.

The composition-coated substrate may be positioned within an electromagnetic radiation curing apparatus, such as the "ZETA" 7200 ultraviolet curing chamber or the "UVALOC" 1000 ultraviolet curing chamber, equipped with an appropriate source of electromagnetic radiation, such as ultraviolet radiation, at an appropriate distance therefrom, such as within the range of about 1 to 2 inches, with about 3 inches being desirable. As noted above, the composition-coated substrate may remain in position or may be passed thereunder at an appropriate rate, such as within the range of about 1 to about 60 seconds per foot, with about 5 seconds per foot. Such passage may occur one or more times, or as needed to effect cure of the composition on the substrate. The length of exposure may be in the range of a few seconds or less (for one time exposure) to tens of seconds or longer (for either a one time exposure or a multiple pass exposure) if desired, depending on the depth of the composition to be cured and of course on the components of the composition themselves.

A reaction product is also of course provided by the teaching of this invention. The reaction product is formed from photocurable compositions after exposure thereof

to electromagnetic radiation sufficient to effect cure of the composition. The reaction product is formed rapidly, and ordinarily and desirably without observed formation of blooming or crazing, see infra.

The reaction product of the photocurable composition may be prepared by dispensing in low viscosity or liquid form a photocurable composition in accordance with present invention onto a substrate and mating that substrate with a second substrate to form an assembly. Thereafter, exposure to electromagnetic radiation on at least one substrate of the assembly for an appropriate period of time should transform the photocurable composition into an adhesive reaction product.

It is also within the scope of the present invention for reaction products to be prepared from a photocurable composition separately from the device, and thereafter positioned on a substrate surface with which it is to be used.

The viscosity of the photocurable composition may be controlled or modified to optimize its dispensability by, in addition to inclusion of an appropriate material to alter the viscosity thereof as noted above, adjusting the temperature of (1) the composition itself, or (2) the substrates on which the composition may be placed to assemble the device. For example, the temperature of the composition or the substrate(s) or combinations thereof may be decreased to increase the viscosity of the composition. In this way, the uniformity on the substrate of the dispensed photocurable composition may be enhanced using lamination techniques, centrifuge techniques, pressure applied from the atmosphere (such as with vacuum bagging), pressure applied from a weighted object, rollers and the like.

The substrates onto which the photocurable compositions of the present invention are intended to be dispensed may be constructed from the litany of materials recited supra, which may be substantially inflexible as well

as flexible. The type of substrate chosen with respect to flexibility will of course depend on the application for which it is to be used. More specifically, the substrates may be constructed from substantially inflexible materials, such as glass, laminated glass, tempered glass, optical plastics, such as polycarbonates, acrylics and polystyrenes, and other alternatives as noted supra; and flexible materials, such as "MYLAR" film or polyolefin, such as polyethylene or polypropylene, tubing.

The choice of substrate material may influence the choice of processing technique used to prepare the photocurable composition into the cured reaction product or the type of device assembled. For example, when assembling a device from at least one flexible substrate, a composition may be advantageously applied to an end portion of the flexible substrate and allowed to wick along that end portion through a portion of another substrate, which is dimensioned to receive that end portion of the flexible substrate. A particular example of such an application is polyolefin tubing intended for medical applications, one end portion of which is dimensioned for receiving by an acrylic luer housing.

Since the photocurable compositions of the present invention cure to form reaction products through a photo-initiated free radical mechanism, the composition is exposed to the source of electromagnetic radiation to effect cure. The choice of substrate may affect the rate and degree at which cure occurs of the photocurable compositions of the present invention. For instance, it is desirable for the substrates to be bonded together to be substantially free of electromagnetic radiation-absorbing capabilities. That is, the greater degree of electromagnetic radiation transmitting capability the substrate possesses, the greater the rate and degree of cure of the composition, all else being equal of course.

It may be desirable to package the inventive compositions in a two part package, particularly in those

instances where a cyanoacrylate component and a non-cyanoacrylate radical curable component are present.

Blooming or crazing may be observed when compositions cure into reaction products and the cure itself is incomplete. That is, blooming refers to the evaporation of cyanoacrylate monomer (due to its relatively high vapor pressure) from uncured fillets, the result of which is formation of a precipitate on surfaces adjacent to the bond line which are also observed as a white haze. Crazing refers to the formation of stress cracks on certain synthetic materials, such as polycarbonates, acrylics and polysulfones, due in this instance to the presence thereon of cyanoacrylate monomer.

The result of incomplete curing may be observed with respect to adhesive uses of the photocurable composition as adhesive or cohesive failure of the cured composition when applied to or between substrates. Such observations may be minimized or even eliminated by using electromagnetic radiation transmitting (as contrasted to absorbing) substrates and placing the source of electromagnetic radiation at a strategic location so as to improve the degree of electromagnetic radiation to which the composition on the substrate is exposed. Similarly, additional sources of electromagnetic radiation, or as stated above reflectors which redirect onto desired portions of the substrate stray or errant electromagnetic radiation, may be employed to further enhance cure.

The compositions of the present invention minimize and often eliminate blooming and crazing in commercial applications of the compositions by curing through the photoinitiated mechanism.

In addition, the compositions of this invention provide a built-in secondary cure system (i.e., photo-initiated free radical initial in addition to the ordinary cyanoacrylate anionic initiation), which is particularly attractive in those applications where certain of the substrates which may be used in the assembly do not allow

the transmission of light, rendering another type of adhesive (such as a dual cure acrylic adhesive) less desirable because a secondary heating step would then be required; elimination of a substrate primer step, which obviates the use of often flammable materials and invites automated processes; and improved cure through volume capabilities.

In view of the above description of the present invention, it is evident that a wide range of practical opportunities is provided by the teaching herein. Certain of those practical opportunities are exemplified below, as are many of the advantages and benefits of the present invention. However, the invention as so exemplified is for illustrative purposes only and is not to be construed in any way as limiting the broad aspects of the teaching herein provided.

EXAMPLES

Example 1

In this example, formulations were prepared to demonstrate the effect of one or the other of a radical initiator component and a photoinitiator component in ether to cyanoacrylate composition. The photoinitiated radical generating component chosen was dibenzoyl peroxide ("DBPO") and the photoinitiator component was 2,4,6-triphenylpyrylium tetraflouroborate ("TPT"). The formulations were prepared by mixing the appropriate components with the cyanoacrylate and thereafter dispensing a drop of the formulation onto a polycarbonate slide. The slide was then exposed to 1000 watts of mercury arc light in a "UVALOC" 1000 irradiation chamber for a period of time of about 30 seconds. The results of this example are shown below in Table 1.

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinititor component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that
vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained

in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of mercury arc light and/or when one drop of the sample was placed on a glass slide and a second glass slide was positioned thereover, and thereafter exposing the single or double glass slide assembly to a Philips lamp HPR125 at 6 mW/cm^2 intensity or to no extra light at all.

Table 2

Sample No.	TPT [ppm]	Radical Initiator		Curing Speed [secs]		
				1000 W 1 glass slide	2 glass slides	
		Type	[ppm]		6 mW/cm^2	No light
14	2000	DBPO	100	29	2	>50
15	2000	DBPO	150	28	2	>50
16	2000	DBPO	250	29	2	>50
17	2000	DBPO	350	31	1-2	>50
18	2000	DBPO	450	31	1-2	>50
19	2000	DBPO	600	34	1-2	>50
20	2000	DBPO	1000	35		
21	2000	DBPO	5000	35		
22	2000	TBPB	600	35		
23	2000	TBPB	1000	35		
24	2000	TBPB	5000	35		
25	2000	DTBPO	400	35		
26	2000	DTBPO	1000	35		
27	2000	DTBPO	5000	35		
28	2000	DEAP	200	40		
29	2000	DEAP	1000	30		
30	2000	DEAP	5000	35		
31	2000	DMPAP	200	35		
32	2000	DMPAP	1000	30		
33	2000	DMPAP	5000	30		
34	2000	ABCH	400	33		
35	2000	ABCH	2000	40		
36	2000	BBPH	400	40		
37	2000	AIBN	100	31	1	>50
38	2000	AIBN	200	31	1-2	>50
39	2000	AIBN	400	29	1-2	>50
40	2000	AIBN	800	30	1-2	>50
41	2000	AIBN	2000	30	2	>50
42	2000	AIBN	4000	31	2-3	>50
43	4000	AIBN	2000	33		
44	4000	AIBN	4000	35		
45	2000	DCPO	200	40		
46	2000	DCPO	1000	35		
47	2000	DCPO	5000	40		
48	2000	ABCV	400	55		
49	2000	ABCV	2000	55		

50	2000	TBHPO	400	50		
51	2000	TBHPO	2000	45		
52	2000	BBPDMH	400	38		
53	2000	BBPDMH	2000	38		
54	2000	BBPDMH	400	35		
55	2000	BBPDMH	2000	40		
56	2000	ADCDP	400	22		
57	2000	ADCDP	2000	15		
58	2000	LPO	400	30		
59	2000	LPO	2000	32		
60	2000	DPTPO	400	35		
61	2000	DPTPO	2000	22		
62	2000	DC	400	45		
63	2000	DC	2000	55		
64	2000	CHPO	400	50		

Table 2 shows that a variety of photoinitiated radical generating components may be used to render a cyanoacrylate-containing formulation photocurable in the presence of a photoinitiator -- in this case TPT. Such photoinitiated radical generating components include, in addition to DBPO, other peroxides, peresters, azo-compounds, halo acetophenones (e.g., DC), aromatic carbonyl compounds (e.g., DMPAP and DEAP), acyl phosphine oxides (e.g., DPTPO) and related compounds.

Example 3

In this example, a variety of different photoinitiator components were chosen for evaluation in an ethyl-2-cyanoacrylate formulation with DBPO as a phtoinitiated radical generating component, with one exception being AIBN in Sample No. 74. The specific photoinitiator components chosen and the amounts used are set forth below in Table 3, as well are the curing speeds of the formulations.

Table 3

Sample No.	Radical Initiator		Photoinitiator		Curing Speed [secs]		
					1000 W 1 slide glass	2 glass slides	
	Type	[ppm]	Type	[ppm]		6 mW/cm^2	No light
65	DBPO	100	TPT	2000	29	2	>50
66	DBPO	150	TPT	2000	28	2	>50
67	DBPO	250	TPT	2000	29	2	>50
68	DBPO	350	TPT	2000	31	1-2	>50
69	DBPO	200	PBT	2000		25	>50
70	DBPO	200	DNT	2000		1	10
71	DBPO	200	DNT	5000	45	1-2	40
72	DBPO	200	TPTS	2000		4	45
73	DBPO	200	TPTS	5000	40	2	>50
74	AIBN	500	DTPT	2000	30	2	>50
75	DBPO	250	DTPT	2000	35	2	>50
76	DBPO	250			>60	>30	>30
77	DBPO	200	CPPP	2000	>50		
78	DBPO	200	CPPP	3000	>50	>50	>50
79	DBPO	200	DMPT	2000	>50	>50	
80	DBPO	200	DMPPC	2000		35	
81	DBPO	200	DMPPC	5000	40	20	20
82	DBPO	200	BHNT	2000		>50	
83	DBPO	200	BHNT	3000	40	45	
84	DBPO	200	DFPT	2000		>50	
85	DBPO	200	DFPT	5000	40	>50	
86	DBPO	250	CBMOC	2000	>60	>50	>50
87	DBPO	250	ADCN	2000	>60	>50	>50

Example 4

In this example, a side-by-side evaluation of a cyanoacrylate composition (one with TPT at a 2000 ppm level and DBPO at a 200 ppm level) curing in the presence of air and in the presence of a nitrogen atmosphere demonstrated that the presence of oxygen inhibits the ability of the composition to cure.

In addition, cyanoacrylate compositions with TPT as a photoinitiator component at 1500 ppm and varied levels of DBPO as a radical initiator component, where the amount was varied, were cured to illustrate that these compositions cure through a free radical initiated mechanism.

In Table 4a below, the effect is shown of increasing the level of DBPO on the cure speed of a composition (Sample No. 65) on a polycarbonate slide when exposed to mercury arc light at an intensity of 1000 W.

Increasing the level of DBPO shows an increase in the time required to achieve a tack free surface from the formulation.

An optimum concentration for the photoinitiated radical generating component may indicate the radical nature of the photocuring effect. That is, at a low concentration, the decay of the photoinitiated radical generating component, e.g., DBPO, triggers the growth of macroradicals; at a higher concentration a part of the DBPO may also quench chain propagation.

Table 4a

DBPO [ppm]	Cure speed @ 1000 W [secs]
100	30
200	25
300	20
400	30
800	45

In Table 4b below, a composition within the scope of this invention (Sample No. 88) was prepared and evaluated for tack free time. A composition having the same radical initiator component and the same photoinitiator component in the same amounts (Sample No. 89) was also prepared, to which was added 2000 ppm of hydroquinone. Hydroquione is a known free radical scavenger. In the table it may be seen that the introduction of the hdroquinone vastly retards, if not completely impedes within a reasonable time period, the ability of the composition to cure when exposed to UV light. This data indicates that the inventive compositions cure through a radical initiated mechanism.

Table 4b

Sample No.	DBPO [ppm]	TPT [ppm]	Tack-free time @ 1000 W [secs]
88	200	2000	26
89	200	2000	>60

Example 5

In this example, a non-cyanoacrylate radical curable component was included with the cyanoacrylate to illustrate the ability of the so-formed formulations to cure when exposed to appropriate radiation in the electromagnetic spectrum. The identity of such components, the percent by weight added and the speed of cure are set forth below in Table 5.

Table 5

Sample No.	Non-Cyanoacrylate Radical Curable Component		Curing speed [secs]
	Type	Amt[%]	
90	--	--	6
91	Styrene	25	6
92	Styrene	50	8
93	Styrene	75	16
94	Tetrahydrofurfuryl methacrylate	25	40
95	Tetrahydrofurfuryl methacrylate	50	32
96	Isodecyl methacrylate	25	15
97	Phenylacetylene	50	18
98	2-Phenylethyl methacrylate	50	34
99	Trimethylphenyl acrylate	50	36
100	Pentaerythritol tetraacrylate	50	12

Example 6

In this example, a variety of photoinitiated radical generating components were added to ethyl-2-cyanoacrylate in various amounts, with and without 2500 ppm of TPT as a photoinitiator, to determine the cure speed after exposure to UV light at an intensity of 1000 W in an irradiation chamber ("UVALOC 1000", Loctite Deutschland GmbH).

More specifically, Sample Nos. 102, 104, 106, 108, 110, 112, 114, 116, 118, and 120 contained TPT.

Table 6

Sample No.	Photoinitiated Radical Generating Component					Curing Time [secs]
	AIBN	LUCIRIN TPO	IRGACURE 184	IRGACURE 651	IRGACURE 907	
101	500					>60
102	500					34
103	20000					*
104	20000					42
105		1500				*
106		1500				26
107		20000				*
108		20000				13
109			1500			*
110			1500			45
111			20000			*
112			20000			>60
113				1500		*
114				1500		50
115				20000		*
116				20000		>60
117					1500	>60
118					1500	4
119					20000	15
120					20000	3

* No curing observed; sample evaporates before curing.

While the present invention has been exemplified as shown above, it is clear that variations are also intended to be within the spirit and scope of the present invention and may be practiced in accordance herewith, with only routine, rather than undue, experimentation. Any variations and equivalents should provide suitable, if not comparable results, when viewed in connection with the results obtained from the above examples. Accordingly, such variations and equivalents are also intended to be encompassed by the claims.

What Is Claimed Is:

1. A photocurable composition comprising:
(a) a 2-cyanoacrylate component,
(b) a photoinitiated radical generating component, and
(c) a photoinitiator component.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by $H_2C=C(CN)-COOR$, wherein R is selected from the group consisting of C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

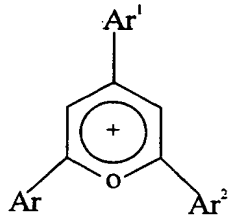
5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclohexane, 2,5-bis(t-butylperoxy)-2,4-

dimethylhexane, bis[1-(t-butylperoxy)-1-methyl-ethyl]benzene, benzoin methylether, cumylhydroperoxide, dibenzoylperoxide, di-t-butylperoxide, 2,2-diethoxyacetophenone, 2,2-dimethoxy-phenylacetophenone, dicumylperoxide, diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide, desylchloride, lauroylperoxide, t-butylperoxybenzoate, t-butylhydroperoxide and combinations thereof.

7. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-, trimethyl pentyl phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-2-methyl-1-phenyl-1-propane, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

8. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of within the following structure:



X^-

wherein each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium

tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to any one of Claims 1-11, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to any one of Claims 1-11, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to any one of Claims 1-14; and

(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to any one of Claims 1-14 in a two-part formulation.

17. The composition according to any one of Claims 1-14 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to any one of Claims 1-14 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to any one of Claims 1-14, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

INTERNATIONAL SEARCH REPORT

Int[redacted]ional application No.
P[redacted]S00/24620

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0; STN CA PLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,139,388 A [REICH et al] 13 February 1979, abstract, col.2, lines 47-57, Example 1, claims 1,2.	1-4, 12/5-9, 14-18 ---------- 1-4, 12/5-9, 14-18
Y	US 5,922,783 A [WOJCIAK] 13 July 1999, abstract, col.3, lines 14-21, 54-64, col.4, lines 41-67, col.5, lines 1-24, 42-45, 53-60, col.6, lines 2220-34, 42-50, col.7, 43-53, Example 1.	1-19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,530,037 A [MCDONELL et al] 25 June 1996, abstract, col.3, lines 60-66, col.4, 5, col.7, lines 14-16, Example 1, claims 1-3, 7, 11, 16, 17.	1-5, 7, 12, 14-18/6, 8-11, 13, 19 ---------- 1-5, 7, 12, 14-18/6, 8-11, 13, 19
A	EP 0 274 595 A (GENERAL ELECTRIC COMPANY) 20 July 1988, entire document.	1-19
A --- Y	US 3,940,362 A [OVERHULTS] 24 February 1976, abstract, col.2, lines 42-45, col.3, lines 15-18, 44-50, col.4, lines 55-60, col.5, lines 10-20, Examples I-XXVI, claims 1-9, 19, 21.	1-19 ----- 1-19
A	US 5,824,180 A [MIKUNI et al] 20 October 1998, entire document	1-19
A --- Y	EP 0 769 721 A (THREE BOND CO., LTD) 23 April 1997, abstract, page 3, page 10, 19-59, page 11, lines 1-5, 40-46, page 12, Table 1.	1-19 ------ 1-19

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(54) Title: RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

(57) Abstract: A radiation-curable composition that includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component, and a photoinitiator component is provided.

RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to radiation-curable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component.

Brief Description of Related Technology

Cyanoacrylates generally are quick setting materials which cure to clear, hard glassy resins, useful as sealants, coatings, and particularly adhesives for bonding together a variety of substrates [see e.g., H.V. Coover, D.W. Dreifus and J.T. O'Connor, "Cyanoacrylate Adhesives" in Handbook of Adhesives, 27, 463-77, I. Skeist, ed., Van Nostrand Reinhold, New York, 3rd ed. (1990)].

Ordinarily, upon contact with substrate materials possessing a surface nucleophile, cyanoacrylate-containing compositions spontaneously polymerize to form a cured material. The cured material exhibits excellent adhesive properties to materials such as metals, plastics, elastomers, fabrics, woods, ceramics and the like.

Cyanoacrylate-containing compositions are thus seen as a versatile class of single-component, ambient temperature curing adhesives.

With conventional polymerizable compositions other than those containing cyanoacrylate monomers, radiation cure generally presents certain advantages over other known cure methods. Those advantages include reduced cure time, solvent elimination (which thereby reduces environmental pollution, and conserves raw materials and energy) and inducement of low thermal stressing of substrate material. Also, room temperature radiation cure prevents degradation of certain heat sensitive polymers, which may occur during a thermal cure procedure.

Radiation-curable, resin-based compositions are legion for a variety of uses in diverse industries, such as coatings, printing, electronic, medical and general engineering. Commonly, radiation-curable compositions are used for adhesives, and certain of the compositions are acrylate-based compositions.

Well-known examples of radiation-curable, acrylate-based resins include those having structural backbones of urethanes, amides, imides, ethers, hydrocarbons, esters and siloxanes. [See e.g., J.G. Woods, "Radiation-Curable Adhesives" in Radiation Curing: Science and Technology, 333-98, 371, S.P. Pappas, ed., Plenum Press, New York (1992).] The common cure mechanism for such radiation-curable, acrylate-based compositions is reported to be free-radical polymerization.

European Patent Publication EP 393 407 describes a radiation-curable composition which includes a slow cure cationic polymerizable epoxide, a fast cure free radical polymerizable acrylic component and a photoinitiator. Upon exposure to radiation, the photoinitiator is said to be capable of generating a cationic species which is capable of initiating polymerization of the epoxide and a free radical species which is capable of initiating polymerization of the acrylic component. The polymerizable acrylic component includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters,

examples of which are expressed as 2-cyanoethyl acrylate (CH_2=$CHCOOCH_2CH_2CN$) and 3-cyanopropyl acrylate (CH_2=$CHCOOCH_2CH_2CH_2CN$). (See page 5, lines 19-26.)

U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

In C. Kutal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^-, cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Kutal) 5,691,113 (Kutal) and 5,877,230 (Kutal).

International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α-cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VII of the periodic table and aromatic electron system ligands selected from π-arenes, indenyl, and η-cyclopentadienyl. The photocurable composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni) describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic

one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition component would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism, thereby providing to the compositions (and cured reaction products formed therefrom) the benefits and

advantages of curing through such a mechanism. More specifically, photocurable compositions of this invention cure rapidly when used, and in so doing minimize the opportunity for undesirable blooming or crazing formation in the cured reaction product. In addition, the inventive photocurable compositions are capable of curing through larger gaps between substrate surfaces than conventional cyanoacrylates, or known photocurable cyanoacrylates. Moreover, as set forth in greater detail below, in one aspect of the invention the photocurable compositions include a non-cyanoacrylate-based radical curable component. The precense of such a component in the inventive compositions allows for the generation of copolymers and reaction products, which would not otherwise be accesible through typical anionic polymerization mechsanisms -- the predominant polymerization of cyanoacrylates.

In another aspect of the present invention, there is provided a method of polymerizing a photocurable composition by providing an amount of the composition to a desired surface and exposing the composition to radiation in an amount sufficient to effect cure thereof.

In yet another aspect of the present invention, there is provided the cured reaction product formed from a photocurable composition after exposure thereof to a curingly effective amount of radiation.

The present invention will be more readily appreciated by those persons of skill in the art based on a reading of the detailed description of the invention which follows and the examples presented thereafter for illustrative purposes.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to photocurable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoiniated radical generating component and a photoinitiator component.

The cyanoacrylate component or cyanoacrylate-containing formulation includes cyanoacrylate monomers which

may be chosen with a raft of substituents, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, such as n-propyl- or i-propyl-2-cyanoacrylate, butyl-2-cyanoacrylates, such as n-butyl- or i-butyl-2-cyanoacyrlate, octyl-2-cyanoacrylates, such as n-alkyl-, 2-alkyl-2-cyanoacrylate, and the like, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable cyanoacrylate monomer for use herein is ethyl-2-cyanoacrylate.

Among the different types of materials appropriate for use as the photoiniated radical generating component desirable ones share at least these common features: they possess electron withdrawing substituents present at at least one portion of the molecule, thereby rendering the portion(s) electron deficient. And when placed in contact with a photoexcitable material (such as a dye), which when exposed to radiation of an appropriate wavelength, absorbs energy sufficient to cause the radical initiator to cleave at the electron deficient portion(s) of the molecule, thereby generating free radicals.

A variety of photoiniated radical generating components are suitable for use herein, such as α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, and peresters. Of course, combinations of these compounds may also be used.

More specific examples of such materials include azoisobutyronitrile ("AIBN"), 1,1'-azo-bis(cyclohexane carbonitrile) ("ABCH"), 4,4'-azo-bis(4-cyanovaleric acid) ("ABCV"), 1,1'-(azodicarbonyl)-dipiperidine ("ADCDP"), 1,1-bis(t-butylperoxy)cyclohexane ("BBPH"), 2,5-bis(t-butylperoxy)2,5-dimethylhexane ("BBPDMH"), bis[1-(t-butylperoxy)-1-methyl-ethyl]benzene ("BBPMEB"), benzoin methylether ("BME"), cumylhydroperoxide ("CHPO"), dibenzoylperoxide ("DBPO"), di-t-butylperoxide ("DTBPO"),

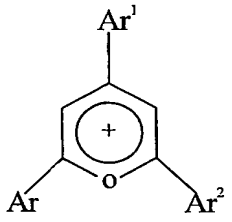
2,2-diethoxyacetophenone ("DEAP"), 2,2-dimethoxy-phenylacetophenone ("DMPAP"), dicumylperoxide ("DCPO"), diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide ("DPTPO"), desylchloride ("DC"), lauroylperoxide ("LPO"), t-butylperoxybenzoate ("TBPB"), and t-butylhydroperoxide ("TBHPO").

Other examples include those available commercially from Ciba Specialty Chemicals Corp., Tarrytown, New York under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl) phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one), and 819 [bis(2,4,6-trimethyl benzoyl) phenyl phosphine oxide] and "DAROCUR" 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and 4265 (the combination of 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one); and the visible light [blue] photoinitiators, dl-camphorquinone and "IRGACURE" 784DC (bis(η^5-2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium).

Of course, combinations of these materials may also be employed herein.

Photoinitiators enhance the rapidity of the curing process when the radiation compositions are exposed to electromagnetic radiation. A number of photoinitiators may be employed herein, examples of which include, but are not limited to,

Photoinitiators useful herein include pyrylium-based materials having a core structure of



X^-

where each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion, such as halogen, hexahalophosphate, hexahaloarsenate, hexahaloantimonate, tetrahaloferrate, tetrahaloborate (e.g., fluoro, chloro, bromo and iodo), and sulfonate.

More specific representations of the pyrylium-based materials include: 2,4,6-triphenylpyrylium-tetrafluoroborate ("TPT"), 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium-tetrafluoroborate) ("PBT"), 2,4-diphenylnaphto-(1,2-B) pyrylium-tetrafluoroborate ("DNT"), 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate ("TPTS"), and 2,6-dipenyl-4(p-tolyl)-pyrylium tetrafluoroborate ("DTPT").

In the aspect of the invention where a non-cyanoacrylate-based radical curable component is included in the inventive compositions, such radical curable component may be selected from a wide variety of materials, such as alkenes or alkynes.

Of these, styrene and derivatives thereof, such as alkyl- and alkenyl-ether derivatives, (meth)acrylates, alkyl- and aryl or alkenyl acetylenes, as well as esters of vinyl alcohol (e.g., vinyl acetate), are particularly desirable.

With respect to formulating photocurable compositions, generally the components may be introduced to one another in any convenient order. Alternatively, it may be desirable to prepare a premix of the radical initiator component and the photoinitiator component. In this way, a ready made premix of those components may be added to the cyanoacrylate component of the formulation to allow for a quick and easy one-part formulation of a photocurable composition prior to dispensing and curing thereof.

For packaging and dispensing purposes, it may be desirable for photocurable compositions in accordance with the present invention to be relatively fluid and flowable. Variations in the viscosity thereof may also be desirable in

certain applications and may be readily achieved through routine changes in formulation, the precise changes being left to those persons of ordinary skill in the art.

For instance, ordinarily cyanoacrylate-containing compositions free from an added thickener or viscosity modifier are low viscosity formulations (such as in the range of 1 to 3 cps). While a composition with such a viscosity (or one whose viscosity has been modified to be up to about five times that viscosity) may be appropriate for a wicking application where a small gap exists between sustrates to be bound (e.g., less than about 0.1 mils) and/or an application where enhanced cure speed is desirable, such a viscosity may be too low for convenient use in certain industrial applications. At least for this reason, the viscosity of cyanoacrylate-containing compositions has at times been desirably modified through, for instance, the addition of polymethylmethacrylates and/or fumed silicas. See e.g., U.S. Patent Nos. 4,533,422 (Litke) and Re. 32,889 (Litke), the disclosures of each of which are hereby expressly incorporated herein by reference.

A medium viscosity formulation (such as in the range of 100 to 300 cps) may be more appropriate in applications where greater control of flowability is desirable. And a high viscosity formulation (such as in the range of 600 to 1000 cps) may be more appropriate in applications involving porous substrates and/or substrates with larger gaps (such as greater than about 0.5 mils).

Of course, those persons of skill in the art should make appropriate decisions regarding whether a viscosity modifier should be included in the photocurable composition, and if so which one(s) and at what level should one be included to achieve the desired viscosity for the intended applications.

In addition, it may be desirable to toughen the cured photocurable compositions of the present invention through the addition of elastomeric rubbers such as is taught by and claimed in U.S. Patent No. 4,440,910 (O'Connor), the disclosure of which is hereby expressly incorporated herein by reference. It may also be desirable

to improve the hot strength of the cured photocurable compositions by addition of anhydrides, such as is taught by and claimed in U.S. Patent No. 4,450,265 (Harris) and the documents cited therein, the disclosures of each of which are hereby expressly incorporated herein by reference.

Moreover, the compositions of the present invention may be rendered into a thixotropic paste through addition of powdered organic fillers having a particle size of about 2 to 200 microns as is taught by U.S. Patent No. 4,105,715 (Gleave) or thickened by a copolymer or terpolymer resin to improve peel strength as is taught by U.S. Patent No. 4,102,945 (Gleave), the disclosures of each of which are hereby incorporated herein by reference.

Further, the compositions of the present invention may be rendered more resistant to thermal degradation at elevated temperature conditions by the inclusion of certain sulfur-containing compounds, such as sulfonates, sulfinates, sulfates, sultones and sulfites as set forth in U.S. Patent No. 5,328,944 (Attarwala), the disclosure of which is hereby expressly incorporated herein by reference. The inclusion of such compounds in the photocurable compositions of the present invention renders those compositions well-suited for applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium

dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a phtotiniated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α-halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phospine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or ketocoumarine derivatives, in an amount within the range of about 0.5% to about 10% by weight of the composition, with about 2% to about 4% or greater by weight of the total composition being desirable. The balance of the composition is composed predominantly of a cyanoacrylate component, such as ethyl-2-cyanoacrylate. Of course, the amount of all the components -- including stabilizers -- together in the composition totals 100%.

A method of curing a photocurable composition in accordance with this invention is also provided herein, the steps of which include (a) providing onto a desired surface an amount of a photocurable composition; and (b) subjecting the composition to radiation sufficient to effect cure thereof.

The amount of photocurable composition provided should be sufficient to cure and form an adequate bond to the substrate surfaces between which it is applied. For instance, application of the photocurable composition may be

achieved by dispensing the composition in drop-wise fashion, or as a liquid stream, brush-applied, dipping, and the like, to form a thin film. Application of the photocurable composition may depend on the flowability or viscosity of the composition. To that end, viscosity modifiers, as noted above, may be included in the composition.

The photocurable compositions of the present invention have taken the ordinary undesirable by-product free radical reaction that compromises shelf life stability and turned it into a controlled free radical cure mechanism.

In use, such compositions are desirably readily dispensed onto a portion of a desired surface of a substrate onto which is to be bonded a portion of another substrate. The photocurable composition may be applied to certain portions of the substrate surface or over the entire surface of the substrate to be bonded, depending on the particular application.

The source of radiation emitting electromagnetic waves is selected from ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof. Desirably, ultraviolet light is the radiation of choice, with appropriate sources including "H", "D", "V", "X", "M" and "A" lamps, mercury arc lamps, and xenon arc lamps (such as those commercially available from Loctite Corporation, Rocky Hill, Connecticut; Fusion UV Curing Systems, Buffalo Grove, Illinois; Spectroline, Westbury, New York; or Xenon Corp., Woburn, Massachusetts; microwave-generated ultraviolet radiation; solar power and fluorescent light sources. Any of these electromagnetic radiation sources may use in conjunction therewith reflectors and/or filters, so as to focus the emitted radiation onto a specific portion of a substrate onto which has been dispensed a photocurable composition and/or within a particular region of the electromagnetic spectrum. Similarly, the electromagnetic radiation may be generated directly in a steady fashion or in an intermittent fashion so as to minimize the degree of heat build-up. Although the electromagnetic radiation employed to cure the photocurable compositions into desired reaction products is often

referred to herein as being in the ultraviolet region, that is not to say that radiation in other regions within the electromagnetic spectrum may not also be suitable. For instance, in certain situations, radiation in the visible region of the electromagnetic spectrum may also be advantageously employed, whether alone or in combination with, for instance, radiation in the ultraviolet region. Of course, microwave and infrared radiation may also be advantageously employed under appropriate conditions.

Higher or lower radiation intensities, greater or fewer exposures thereto and length of exposure and/or greater or lesser distances of the source of radiation to the composition may be required to complete curing, depending of course on the particular components of a chosen composition.

More specifically with respect to radiation intensity, the chosen lamp should have a power rating of at least about 100 watts per inch (about 40 watts per cm), with a power rating of at least about 300 watts per inch (about 120 watts per cm) being particularly desirable. Also, since the inclusion of a photoinitiator in the composition may shift the wavelength within the electromagnetic radiation spectrum at which cure occurs, it may be desirable to use a source of electromagnetic radiation whose variables (e.g., wavelength, distance, and the like) are readily adjustable.

During the curing process, the composition will be exposed to a source of electromagnetic radiation that emits an amount of energy, measured in mW/cm^2, determined by parameters including: the size, type and geometry of the source; the duration of the exposure to electromagnetic radiation; the intensity of the radiation (and that portion of radiation emitted within the region appropriate to effect curing); the absorbency of electromagnetic radiation by any intervening materials, such as substrates; and the distance the composition lies from the source of radiation. Those persons of skill in the art should readily appreciate that curing of the composition may be optimized by choosing appropriate values for these parameters in view of the particular components of the composition.

To effect cure, the source of electromagnetic radiation may remain stationary while the composition passes through its path. Alternatively, a substrate coated with the photocurable composition may remain stationary while the source of electromagnetic radiation passes thereover or therearound to complete the transformation from composition to reaction product. Still alternatively, both may traverse one another, or for that matter remain stationary, provided that the photocurable composition is exposed to electromagnetic radiation sufficient to effect cure.

Commercially available curing systems, such as the "ZETA" 7200 or 7400 ultraviolet curing chamber (Loctite Corporation, Rocky Hill, Connecticut), "UVALOC" 1000 (Loctite Deutschland GmbH, Münich, Germany), Fusion UV Curing Systems F-300 B (Fusion UV Curing Systems, Buffalo Grove, Illinois), Hanovia UV Curing System (Hanovia Corp., Newark, New Jersey), BlackLight Model B-100 (Spectroline, Westbury, New York), and RC500 A Pulsed UV Curing System (Xenon Corp., Woburn, Massachusetts), are well-suited for the purposes described herein. Also, a Sunlighter UV chamber fitted with low intensity mercury vapor lamps and a turntable may be employed herein.

The required amount of energy may be delivered by exposing the composition to a less powerful intensity of electromagnetic radiation for a longer period of time, through for example multiple passes, or alternatively, by exposing the composition to a more powerful intensity of electromagnetic radiation for a shorter period of time. In addition, each of those multiple passes may occur with an intensity at different energy intensities. In any event, those persons of skill in the art should choose an appropriate intensity of electromagnetic radiation depending on the particular composition, and position the source of electronic radiation at a suitable distance therefrom which, together with the length of exposure, optimizes transformation. Also, it may be desirable to use a source of electromagnetic radiation that is delivered in an intermittent fashion, such as by pulsing or strobing, so as

to ensure a thorough and complete cure without causing excessive heat build-up.

In use, a photocurable composition in accordance with the present invention may be dispensed, such as in the form of a thin film or droplet, onto a desired substrate. Substrates onto which the photocurable composition of the present invention may be applied may be chosen from a vast selection of different materials; basically, any material with which cyanoacrylates may be used is suitable as well for use herein. See supra.

Desirable choices among such materials include acrylics, epoxies, polyolefins, polycarbonates, polysulfones (e.g., polyether sulfone), polyvinyl acetates, polyamides, polyetherimides, polyimides and derivatives and co-polymers thereof with which may be blended or compounded traditional additives for aiding processibility or modifying the physical properties and characteristics of the material to be used as a substrate. Examples of co-polymers which may be employed as substrates include acrylonitrile-butadiene-styrene, styrene-acrylonitrile cellulose, aromatic copolyesters based on terephthallic acid, *p,p*-dihydroxybiphenyl and *p*-hydroxy benzoic acid, polyalkylene (such as polybutylene or polyethylene) terephthalate, polymethyl pentene, polyphenylene oxide or sulfide, polystyrene, polyurethane, polyvinylchloride, and the like. Of course, other materials may also be employed for use herein. Particularly, desirable co-polymers include those which are capable of transmitting UV and/or visible radiation.

The composition-coated substrate may be positioned within an electromagnetic radiation curing apparatus, such as the "ZETA" 7200 ultraviolet curing chamber or the "UVALOC" 1000 ultraviolet curing chamber, equipped with an appropriate source of electromagnetic radiation, such as ultraviolet radiation, at an appropriate distance therefrom, such as within the range of about 1 to 2 inches, with about 3 inches being desirable. As noted above, the composition-coated substrate may remain in position or may be passed

thereunder at an appropriate rate, such as within the range of about 1 to about 60 seconds per foot, with about 5 seconds per foot. Such passage may occur one or more times, or as needed to effect cure of the composition on the substrate. The length of exposure may be in the range of a few seconds or less (for one time exposure) to tens of seconds or longer (for either a one time exposure or a multiple pass exposure) if desired, depending on the depth of the composition to be cured and of course on the components of the composition themselves.

A reaction product is also of course provided by the teaching of this invention. The reaction product is formed from photocurable compositions after exposure thereof to electromagnetic radiation sufficient to effect cure of the composition. The reaction product is formed rapidly, and ordinarily and desirably without observed formation of blooming or crazing, see infra.

The reaction product of the photocurable composition may be prepared by dispensing in low viscosity or liquid form a photocurable composition in accordance with present invention onto a substrate and mating that substrate with a second substrate to form an assembly. Thereafter, exposure to electromagnetic radiation on at least one substrate of the assembly for an appropriate period of time should transform the photocurable composition into an adhesive reaction product.

It is also within the scope of the present invention for reaction products to be prepared from a photocurable composition separately from the device, and thereafter positioned on a substrate surface with which it is to be used.

The viscosity of the photocurable composition may be controlled or modified to optimize its dispensability by, in addition to inclusion of an appropriate material to alter the viscosity thereof as noted above, adjusting the temperature of (1) the composition itself, or (2) the substrates on which the composition may be placed to assemble the device. For example, the temperature of the composition or the substrate(s) or combinations thereof may

be decreased to increase the viscosity of the composition. In this way, the uniformity on the substrate of the dispensed photocurable composition may be enhanced using lamination techniques, centrifuge techniques, pressure applied from the atmosphere (such as with vacuum bagging), pressure applied from a weighted object, rollers and the like.

The substrates onto which the photocurable compositions of the present invention are intended to be dispensed may be constructed from the litany of materials recited supra, which may be substantially inflexible as well as flexible. The type of substrate chosen with respect to flexibility will of course depend on the application for which it is to be used. More specifically, the substrates may be constructed from substantially inflexible materials, such as glass, laminated glass, tempered glass, optical plastics, such as polycarbonates, acrylics and polystyrenes, and other alternatives as noted supra; and flexible materials, such as "MYLAR" film or polyolefin, such as polyethylene or polypropylene, tubing.

The choice of substrate material may influence the choice of processing technique used to prepare the photocurable composition into the cured reaction product or the type of device assembled. For example, when assembling a device from at least one flexible substrate, a composition may be advantageously applied to an end portion of the flexible substrate and allowed to wick along that end portion through a portion of another substrate, which is dimensioned to receive that end portion of the flexible substrate. A particular example of such an application is polyolefin tubing intended for medical applications, one end portion of which is dimensioned for receiving by an acrylic luer housing.

Since the photocurable compositions of the present invention cure to form reaction products through a photo-initiated free radical mechanism, the composition is exposed to the source of electromagnetic radiation to effect cure. The choice of substrate may affect the rate and degree at which cure occurs of the photocurable compositions of the

present invention. For instance, it is desirable for the substrates to be bonded together to be substantially free of electromagnetic radiation-absorbing capabilities. That is, the greater degree of electromagnetic radiation transmitting capability the substrate possesses, the greater the rate and degree of cure of the composition, all else being equal of course.

It may be desirable to package the inventive compositions in a two part package, particularly in those instances where a cyanoacrylate component and a non-cyanoacrylate radical curable component are present.

Blooming or crazing may be observed when compositions cure into reaction products and the cure itself is incomplete. That is, blooming refers to the evaporation of cyanoacrylate monomer (due to its relatively high vapor pressure) from uncured fillets, the result of which is formation of a precipitate on surfaces adjacent to the bond line which are also observed as a white haze. Crazing refers to the formation of stress cracks on certain synthetic materials, such as polycarbonates, acrylics and polysulfones, due in this instance to the presence thereon of cyanoacrylate monomer.

The result of incomplete curing may be observed with respect to adhesive uses of the photocurable composition as adhesive or cohesive failure of the cured composition when applied to or between substrates. Such observations may be minimized or even eliminated by using electromagnetic radiation transmitting (as contrasted to absorbing) substrates and placing the source of electromagnetic radiation at a strategic location so as to improve the degree of electromagnetic radiation to which the composition on the substrate is exposed. Similarly, additional sources of electromagnetic radiation, or as stated above reflectors which redirect onto desired portions of the substrate stray or errant electromagnetic radiation, may be employed to further enhance cure.

The compositions of the present invention minimize and often eliminate blooming and crazing in commercial

applications of the compositions by curing through the photoinitiated mechanism.

In addition, the compositions of this invention provide a built-in secondary cure system (i.e., photo-initiated free radical initial in addition to the ordinary cyanoacrylate anionic initiation), which is particularly attractive in those applications where certain of the substrates which may be used in the assembly do not allow the transmission of light, rendering another type of adhesive (such as a dual cure acrylic adhesive) less desirable because a secondary heating step would then be required; elimination of a substrate primer step, which obviates the use of often flammable materials and invites automated processes; and improved cure through volume capabilities.

In view of the above description of the present invention, it is evident that a wide range of practical opportunities is provided by the teaching herein. Certain of those practical opportunities are exemplified below, as are many of the advantages and benefits of the present invention. However, the invention as so exemplified is for illustrative purposes only and is not to be construed in any way as limiting the broad aspects of the teaching herein provided.

EXAMPLES

Example 1

In this example, formulations were prepared to demonstrate the effect of one or the other of a radical initiator component and a photoinitiator component in ether to cyanoacrylate composition. The photoinitiated radical generating component chosen was dibenzoyl peroxide ("DBPO") and the photoinitiator component was 2,4,6-triphenylpyrylium tetraflouroborate ("TPT"). The formulations were prepared by mixing the appropriate components with the cyanoacrylate and thereafter dispensing a drop of the formulation onto a polycarbonate slide. The slide was then exposed to 1000

watts of mercury arc light in a "UVALOC" 1000 irradiation chamber for a period of time of about 30 seconds. The results of this example are shown below in Table 1.

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinititor component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that
vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and

amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of mercury arc light and/or when one drop of the sample was placed on a glass slide and a second glass slide was positioned thereover, and thereafter exposing the single or double glass slide assembly to a Philips lamp HPR125 at 6 mW/cm^2 intensity or to no extra light at all.

Table 2

Sample No.	TPT [ppm]	Radical Initiator		Curing Speed [secs]		
				1000 W 1 glass slide	2 glass slides	
		Type	[ppm]		6 mW/cm^2	No light
14	2000	DBPO	100	29	2	>50
15	2000	DBPO	150	28	2	>50
16	2000	DBPO	250	29	2	>50
17	2000	DBPO	350	31	1-2	>50
18	2000	DBPO	450	31	1-2	>50
19	2000	DBPO	600	34	1-2	>50
20	2000	DBPO	1000	35		
21	2000	DBPO	5000	35		
22	2000	TBPB	600	35		
23	2000	TBPB	1000	35		
24	2000	TBPB	5000	35		
25	2000	DTBPO	400	35		
26	2000	DTBPO	1000	35		
27	2000	DTBPO	5000	35		
28	2000	DEAP	200	40		
29	2000	DEAP	1000	30		
30	2000	DEAP	5000	35		
31	2000	DMPAP	200	35		
32	2000	DMPAP	1000	30		
33	2000	DMPAP	5000	30		
34	2000	ABCH	400	33		
35	2000	ABCH	2000	40		
36	2000	BBPH	400	40		
37	2000	AIBN	100	31	1	>50
38	2000	AIBN	200	31	1-2	>50
39	2000	AIBN	400	29	1-2	>50
40	2000	AIBN	800	30	1-2	>50
41	2000	AIBN	2000	30	2	>50
42	2000	AIBN	4000	31	2-3	>50
43	4000	AIBN	2000	33		
44	4000	AIBN	4000	35		
45	2000	DCPO	200	40		
46	2000	DCPO	1000	35		
47	2000	DCPO	5000	40		

48	2000	ABCV	400	55		
49	2000	ABCV	2000	55		
50	2000	TBHPO	400	50		
51	2000	TBHPO	2000	45		
52	2000	BBPDMH	400	38		
53	2000	BBPDMH	2000	38		
54	2000	BBPDMH	400	35		
55	2000	BBPDMH	2000	40		
56	2000	ADCDP	400	22		
57	2000	ADCDP	2000	15		
58	2000	LPO	400	30		
59	2000	LPO	2000	32		
60	2000	DPTPO	400	35		
61	2000	DPTPO	2000	22		
62	2000	DC	400	45		
63	2000	DC	2000	55		
64	2000	CHPO	400	50		

Table 2 shows that a variety of photoinitiated radical generating components may be used to render a cyanoacrylate-containing formulation photocurable in the presence of a photoinitiator -- in this case TPT. Such photoinitiated radical generating components include, in addition to DBPO, other peroxides, peresters, azo-compounds, halo acetophenones (e.g., DC), aromatic carbonyl compounds (e.g., DMPAP and DEAP), acyl phosphine oxides (e.g., DPTPO) and related compounds.

Example 3

In this example, a variety of different photoinitiator components were chosen for evaluation in an ethyl-2-cyanoacrylate formulation with DBPO as a phtoinitiated radical generating component, with one exception being AIBN in Sample No. 74. The specific photoinitiator components chosen and the amounts used are set forth below in Table 3, as well are the curing speeds of the formulations.

Table 3

Sample No.	Radical Initiator		Photoinitiator		Curing Speed [secs]		
					1000 W 1 slide glass	2 glass slides	
	Type	[ppm]	Type	[ppm]		6 mW/cm^2	No light
65	DBPO	100	TPT	2000	29	2	>50
66	DBPO	150	TPT	2000	28	2	>50
67	DBPO	250	TPT	2000	29	2	>50
68	DBPO	350	TPT	2000	31	1-2	>50
69	DBPO	200	PBT	2000		25	>50
70	DBPO	200	DNT	2000		1	10
71	DBPO	200	DNT	5000	45	1-2	40
72	DBPO	200	TPTS	2000		4	45
73	DBPO	200	TPTS	5000	40	2	>50
74	AIBN	500	DTPT	2000	30	2	>50
75	DBPO	250	DTPT	2000	35	2	>50
76	DBPO	250			>60	>30	>30
77	DBPO	200	CPPP	2000	>50		
78	DBPO	200	CPPP	3000	>50	>50	>50
79	DBPO	200	DMPT	2000	>50	>50	
80	DBPO	200	DMPPC	2000		35	
81	DBPO	200	DMPPC	5000	40	20	20
82	DBPO	200	BHNT	2000		>50	
83	DBPO	200	BHNT	3000	40	45	
84	DBPO	200	DFPT	2000		>50	
85	DBPO	200	DFPT	5000	40	>50	
86	DBPO	250	CBMOC	2000	>60	>50	>50
87	DBPO	250	ADCN	2000	>60	>50	>50

Example 4

In this example, a side-by-side evaluation of a cyanoacrylate composition (one with TPT at a 2000 ppm level and DBPO at a 200 ppm level) curing in the presence of air and in the presence of a nitrogen atmosphere demonstrated that the presence of oxygen inhibits the ability of the composition to cure.

In addition, cyanoacrylate compositions with TPT as a photoinitiator component at 1500 ppm and varied levels of DBPO as a radical initiator component, where the amount was varied, were cured to illustrate that these compositions cure through a free radical initiated mechanism.

In Table 4a below, the effect is shown of increasing the level of DBPO on the cure speed of a composition (Sample No. 65) on a polycarbonate slide when exposed to mercury arc light at an intensity of 1000 W. Increasing the level of DBPO shows an increase in the time

required to achieve a tack free surface from the formulation.

An optimum concentration for the photoinitiated radical generating component may indicate the radical nature of the photocuring effect. That is, at a low concentration, the decay of the photoinitiated radical generating component, e.g., DBPO, triggers the growth of macroradicals; at a higher concentration a part of the DBPO may also quench chain propagation.

Table 4a

DBPO [ppm]	Cure speed @ 1000 W [secs]
100	30
200	25
300	20
400	30
800	45

In Table 4b below, a composition within the scope of this invention (Sample No. 88) was prepared and evaluated for tack free time. A composition having the same radical initiator component and the same photoinitiator component in the same amounts (Sample No. 89) was also prepared, to which was added 2000 ppm of hydroquinone. Hydroquione is a known free radical scavenger. In the table it may be seen that the introduction of the hdroquinone vastly retards, if not completely impedes within a reasonable time period, the ability of the composition to cure when exposed to UV light. This data indicates that the inventive compositions cure through a radical initiated mechanism.

Table 4b

Sample No.	DBPO [ppm]	TPT [ppm]	Tack-free time @ 1000 W [secs]
88	200	2000	26
89	200	2000	>60

Example 5

In this example, a non-cyanoacrylate radical curable component was included with the cyanoacrylate to illustrate the ability of the so-formed formulations to cure when exposed to appropriate radiation in the electromagnetic spectrum. The identity of such components, the percent by weight added and the speed of cure are set forth below in Table 5.

Table 5

Sample No.	Non-Cyanoacrylate Radical Curable Component		Curing speed [secs]
	Type	Amt[%]	
90	--	--	6
91	Styrene	25	6
92	Styrene	50	8
93	Styrene	75	16
94	Tetrahydrofurfuryl methacrylate	25	40
95	Tetrahydrofurfuryl methacrylate	50	32
96	Isodecyl methacrylate	25	15
97	Phenylacetylene	50	18
98	2-Phenylethyl methacrylate	50	34
99	Trimethylphenyl acrylate	50	36
100	Pentaerythritol tetraacrylate	50	12

Example 6

In this example, a variety of photoinitiated radical generating components were added to ethyl-2-cyanoacrylate in various amounts, with and without 2500 ppm of TPT as a photoinitiator, to determine the cure speed after exposure to UV light at an intensity of 1000 W in an irradiation chamber ("UVALOC 1000", Loctite Deutschland GmbH).

More specifically, Sample Nos. 102, 104, 106, 108, 110, 112, 114, 116, 118, and 120 contained TPT.

Table 6

Sample No.	Photoinitiated Radical Generating Component					Curing Time [secs]
	AIBN	LUCIRIN TPO	IRGACURE 184	IRGACURE 651	IRGACURE 907	
101	500					>60
102	500					34
103	20000					*
104	20000					42
105		1500				*
106		1500				26
107		20000				*
108		20000				13
109			1500			*
110			1500			45
111			20000			*
112			20000			>60
113				1500		*
114				1500		50
115				20000		*
116				20000		>60
117					1500	>60
118					1500	4
119					20000	15
120					20000	3

* No curing observed; sample evaporates before curing.

While the present invention has been exemplified as shown above, it is clear that variations are also intended to be within the spirit and scope of the present invention and may be practiced in accordance herewith, with only routine, rather than undue, experimentation. Any variations and equivalents should provide suitable, if not comparable results, when viewed in connection with the results obtained from the above examples. Accordingly, such variations and equivalents are also intended to be encompassed by the claims.

What Is Claimed Is:

1. A photocurable composition comprising:
   (a) a 2-cyanoacrylate component,
   (b) a photoinitiated radical generating component, and
   (c) a photoinitiator component.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by $H_2C=C(CN)-COOR$, wherein R is selected from the group consisting of C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

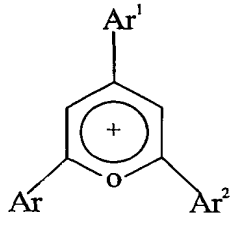
5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclohexane, 2,5-bis(t-butylperoxy)-2,4-dimethylhexane, bis[1-(t-butylperoxy)-1-methyl-

ethyl]benzene, benzoin methylether, cumylhydroperoxide, dibenzoylperoxide, di-t-butylperoxide, 2,2-diethoxyacetophenone, 2,2-dimethoxy-phenylacetophenone, dicumylperoxide, diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide, desylchloride, lauroylperoxide, t-butylperoxybenzoate, t-butylhydroperoxide and combinations thereof.

7. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-, trimethyl pentyl phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-2-methyl-1-phenyl-1-propane, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

8. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of within the following structure:



X^-

wherein each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane

sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to any one of Claims 1-11, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to any one of Claims 1-11, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to any one of Claims 1-14; and

(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to any one of Claims 1-14 in a two-part formulation.

17. The composition according to any one of Claims 1-14 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to any one of Claims 1-14 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to any one of Claims 1-14, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24620

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08F 2/50, 236/12, 2/50, 4/42; C09J 7/04, 4/04

US CL : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0; STN CA PLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,139,388 A [REICH et al] 13 February 1979, abstract, col.2, lines 47-57, Example 1, claims 1,2.	1-4, 12/5-9, 14-18 --- 1-4, 12/5-9, 14-18
Y	US 5,922,783 A [WOJCIAK] 13 July 1999, abstract, col.3, lines 14-21, 54-64, col.4, lines 41-67, col.5, lines 1-24, 42-45, 53-60, col.6, lines 2220-34, 42-50, col.7, 43-53, Example 1.	1-19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 11 OCTOBER 2000	Date of mailing of the international search report 12 MAR 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA Telephone No. (703) 308-8819

Form PCT/ISA/210 (second sheet) (July 1998)★

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,530,037 A [MCDONELL et al] 25 June 1996, abstract, col.3, lines 60-66, col.4, 5, col.7, lines 14-16, Example 1, claims 1-3, 7, 11, 16, 17.	1-5, 7, 12, 14-18/6, 8-11, 13, 19 ---------- 1-5, 7, 12, 14-18/6, 8-11, 13, 19
A	EP 0 274 595 A (GENERAL ELECTRIC COMPANY) 20 July 1988, entire document.	1-19
A --- Y	US 3,940,362 A [OVERHULTS] 24 February 1976, abstract, col.2, lines 42-45, col.3, lines 15-18, 44-50, col.4, lines 55-60, col.5, lines 10-20, Examples I-XXVI, claims 1-9, 19, 21.	1-19 ----- 1-19
A	US 5,824,180 A [MIKUNI et al] 20 October 1998, entire document	1-19
A --- Y	EP 0 769 721 A (THREE BOND CO., LTD) 23 April 1997, abstract, page 3, page 10, 19-59, page 11, lines 1-5, 40-46, page 12, Table 1.	1-19 ------ 1-19

16

PATENT COOPERATION TREATY

PCT

REC'D 27 NOV 2001
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference ICC-211/PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/24620	International filing date *(day/month/year)* 08 SEPTEMBER 2000	Priority date *(day/month/year)* 09 SEPTEMBER 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant LOCTITE CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   I [X] Basis of the report

   II [ ] Priority

   III [ ] Non-establishment of report with regard to novelty, inventive step or industrial applicability

   IV [ ] Lack of unity of invention

   V [X] Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI [ ] Certain documents cited

   VII [ ] Certain defects in the international application

   VIII [ ] Certain observations on the international application

Date of submission of the demand	Date of completion of this report
30 MARCH 2001	18 OCTOBER 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-0651

Form PCT/IPEA/409 (cover sheet) (July 1998)*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/24620

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed

☒ the description:
pages (See Attached), as originally filed
pages ____, filed with the demand
pages ____, filed with the letter of ____

☒ the claims:
pages (See Attached), as originally filed
pages ____, as amended (together with any statement) under Article 19
pages ____, filed with the demand
pages ____, filed with the letter of ____

☒ the drawings:
pages (See Attached), as originally filed
pages ____, filed with the demand
pages ____, filed with the letter of ____

☒ the sequence listing part of the description:
pages (See Attached), as originally filed
pages ____, filed with the demand
pages ____, filed with the letter of ____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language ____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. 8

☒ the drawings, sheets/~~fig~~ NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/24620

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	5-7,9, 10-20	YES
	Claims	1-4, 12	NO
Inventive Step (IS)	Claims	NONE	YES
	Claims	1-7, 9-19	NO
Industrial Applicability (IA)	Claims	1-7, 9-19	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-7, 9-19 lack an inventive step under PCT Article 33(3) as obvous over McDONNELL et al (U.S. 5,530,037)

McDONNELL discloses a curable cyanoacrylate adhesive composition intended for medical and/or veterinary uses is sterilized in liquid form by gamma irradiation. The composition comprises

a) a cyanoacrylate monomer

b) a combination of an anionic stabilizer and a free-radical stabilizer in amounts effective to stabilize the composition during irradiation and to stabilize the sterilized composition during storage prior to cure, wherein the free radical stabilizer is a selected phenolic antioxidant (abstract, col.3, lines 60-66). Phenolic antioxidant is presented by compounds of formula (I), (col. 4, lines 1-5), which depicts a p-benzoquinone.

The cyanoacrylate monomer may be selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl,tert-butyl, n-pentyl, iso-pentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, allyl, methoxyethyl,ethoxyethyl, 3-methoxybutyl and methoxyisopropyl cyanoacrylate esters (col. 4, lines 61-67).

One of preferred antioxidants is butyl hydroxy toluene (BHT, or 4-methyl-2,6-di-tert-butylphenol

Other anti-oxidants which may be used include methyl hydroquinone, catechol, tert-butyl hydroquinone, 4-tert-butoxyphenol, 4-ethoxyphenol, 3-methoxyphenol, 2-tert-butyl-4-methoxyphenol, and 2,2-methylene-bis-(4-methyl-6-tert-butylphenol).

Anionic (acid) stabilizers for cyanoacrylate adhesives include Sulphur Dioxide, Sulphonic Acids, Sulphuric Acid, Sulphur Trioxide, Phosphorous Acids, Carboxylic Acids, Picric Acid, Boron Trifluoride, etc. (col. 5, lines 35-66, col. 6, lines 1-5.

In specific regard toclaims 6, 8-11
McDONNELL discloses a cyanoacrylate adhesives as instantly (Continued on Supplemental Sheet.)

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

CLASSIFICATION:
The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): C08F 2/50, 236/12, 2/50, 4/42; C09J 7/04 and US Cl.: 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,
page(s) 1, 2, 5-10, 12-20, 22-27, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
3, 4, 11, 21, filed with the letter of 13 August 2001

This report has been drawn on the basis of the claims,
page(s) NONE, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) NONE, filed with the demand.
and additional amendments:
28-31, filed with the letter 13 August 2001

This report has been drawn on the basis of the drawings,
page(s) NONE, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
claimed, however does not disclose the same photoinitiators, as per instant claims 6, 8-11. Because the polymerization of MCDONNEL takes place under gamma-irradiation, one skilled in the art would have found it obvious to introduce imitators capable of producing radicals under irradiation with very short wavelength, which are mostly the instantly claimed compounds, and thus to arrive at the instant claims.

Claims 1-7, 9 lack an inventive step under PCT Article 33(3) as being obvious over WOJCIAK (U.S. 5,922,783).
WOJCIAK discloses radiation-curable composition which includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a metallocene component and a polymerizingly effective amount of a photoinitiator to accelerate the rate of cure (abstract).

The cyanoacrylate monomer is selected from methyl cyanoacrylate, 2-ethyl cyanoacrylate, 2-propyl cyanoacrylate, 2-butyl cyanoacrylate, 2-octyl cyanoacrylate, allyl cyanoacrylate, beta-methoxyethyl cyanoacrylate and combination thereof. A particularly desirable cyanoacrylate monomer for use herein is 2-ethyl cyanoacrylate (col. 3, lines 54-66).
A number of photoinitiators are employed by WOJCIAK
Such materials include, but are not limited to, photoinitiators available commercially from Ciba-Geigy Corp.,under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369(2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) and "DAROCUR" 1173 (2-hydroxy-2-methyl-1phenyl-1-propane) and 4265 (the combination of 2,4,6trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy 2-methyl-1-phenyl-propan-1-one); photoinitiators vailable commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn. under the "CYRACURE". The

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

list of photoinitiators, which clearly overlaps with the instantly claimed photoinitiators, is presented in col. 4, lines 41-67, col.5, lines 1-24.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one, free-radical polymerization is also known to occur in this regard under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, however, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive formulations to extend their shelf life. Thus Example 1, col. 10, 11 teaches the following:

> A photocurable composition in accordance with the present invention was prepared from about 95.9 grams of 2-ethyl cyanoacrylate, about 0.1 grams of ferrocene and about 4 grams of "DAROCUR" 1173 as a photoinitiator. Typically, commercially available cyanoacrylate-containing compositions (such as "PRISM" Adhesive 4061, commercially available from Loctite Corporation, Rocky Hill, Conn.) are stabilized against free-radical formation by the addition of an acidic material, such as boron trifluoride or methane sulfonic acid. In this example, therefore, the ethyl cyanoacrylate contained about 20 ppm of boron trifluoride as an acid anionic stabilizer.

Although not all the groups of photoinitiators are disclosed by WOJCIAK, he motivates one skilled in the art to utilize stabilizers, comprising complexes of boron tetrafluoride and stabilizers against free radical formation as instantly claimed.

Claims 112 meet the criteria set out in PCT Article 33(4) for industrial applicability , the compositions as claimed are used as cyanoacrylate adhesives.

Response to Arguments

Applicants' arguments were fully considred, but they are not persuasive. Since the reference to REICH was removed from the scope of rejection, Examiner does not address the arguments on this reference. In regard to McDONALD reference the very first word of the abstarct cites "curable adhesive compositions comprising cyanoacrylate monomer, combination of stabilizers including a compound capable of generating free radicals

As for Applicant's arguments about the intended use of the instant composition compare to that of McDonald, it is well set that a new use of otherwise known or obvious composition does not impact its patentability.

In regard to WOJCIAK reference, which in fact uses the mixture of a metallocene and a free radical component, Examiner notices, that first of all the transitional word "comprising",as per instant claim 1 leaves the possibility of the presence of any other components, even in the major amounts. Secondly, the rejection was made as an obviousness rejection, not as anticipation one, and as shown above reference itself suggests to one skilled in the art the particularities of the instantly claimed composition.

---------- NEW CITATIONS ----------
NONE

includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters, examples of which are expressed as 2-cyanoethyl acrylate (CH_2=CHCOOCH_2CH_2CN) and 3-cyanopropyl acrylate (CH_2=CHCOOCH_2CH_2CH_2CN). (See page 5, lines 19-26.)

U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

In C. Kutal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^-, cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Kutal) 5,691,113 (Kutal) and 5,877,230 (Kutal).

International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α-cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VIII of the periodic table and aromatic electron system ligands selected from π-arenes, indenyl, and η-cyclopentadienyl. The photocurable composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni) describes such compositions in the context of a method of bonding artificial nails.

describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional

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applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a photoinitiated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α-halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phospine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinititor component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of

What Is Claimed Is:

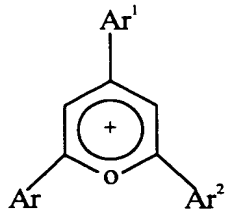
1. A photocurable composition comprising:

(a) a 2-cyanoacrylate component,

(b) a photoinitiated radical generating component, and

(c) a photoinitiator component,

wherein the photoinitator component is selected from the compounds within the following structure:



wherein each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by $H_2C=C(CN)-COOR$, wherein R is selected from the group consisting of C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclchexane, 2,5-bis(t-butylperoxy)-2,4-

7. (Amended) The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-trimethyl pentyl phosphine oxide, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to Claim 1, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to Claim 1, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to Claim 1; and

(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to Claim 1 in a two-part formulation.

17. The composition according to Claim 1 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to Claim 1 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to Claim 1, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 19 June 2001 (19.06.01)	
International application No. PCT/US00/24620	**Applicant's or agent's file reference** ICC-211/PCT
International filing date (day/month/year) 08 September 2000 (08.09.00)	**Priority date** (day/month/year) 09 September 1999 (09.09.99)
Applicant MISIAK, Hanns, R.	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

30 March 2001 (30.03.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Claudio Borton
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

ICC-211/PCT

PCT REQUEST

Original (for **SUBMISSION**) - printed on 07.09.2000 01:22:07 PM

0 0-1	**For receiving Office use only** International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4 0-4-1	**Form - PCT/RO/101 PCT Request** Prepared using	PCT-EASY Version 2.90 (updated 08.03.2000)
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	**Applicant's or agent's file reference**	ICC-211/PCT
I	**Title of invention**	RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS
II II-1 II-2 II-4 II-5 II-6 II-7 II-8 II-9 II-10	**Applicant** This person is: Applicant for Name Address: State of nationality State of residence Telephone No. Facsimile No. e-mail	applicant only all designated States except US LOCTITE CORPORATION 1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America US US (860) 571-5100 (860) 571-5465 steve.bauman@loctite.com
III-1 III-1-1 III-1-2 III-1-4 III-1-5 III-1-6 III-1-7	**Applicant and/or inventor** This person is: Applicant for Name (LAST, First) Address: State of nationality State of residence	applicant and inventor US only MISIAK, Hanns, R. 22 Cypress Avenue/Scholarstown Road 24 Dublin Ireland DE IE

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IV-1	**Agent or common representative; or address for correspondence** The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	BAUMAN, Steven, C.
IV-1-2	Address:	LOCTITE CORPORATION 1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America
IV-1-3	Telephone No.	(860) 571-5001
IV-1-4	Facsimile No.	(860) 571-5028
IV-1-5	e-mail	steve.bauman@loctite.com
V	**Designation of States**	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW
V-5	**Precautionary Designation Statement** In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	

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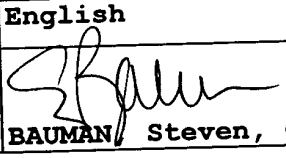
V-6	**Exclusion(s) from precautionary designations**	**NONE**	
VI-1	**Priority claim of earlier national application**		
VI-1-1	Filing date	09 September 1999 (09.09.1999)	
VI-1-2	Number	60/152,945	
VI-1-3	Country	US	
VII-1	**International Searching Authority Chosen**	United States Patent and Trademark Office (USPTO) (ISA/US)	
VII-2	**Request to use results of earlier search; reference to that search**		
VII-2-1	Date		
VII-2-2	Number		
VII-2-3	Country (or regional Office)	US	
VIII	**Check list**	number of sheets	electronic file(s) attached
VIII-1	Request	4	-
VIII-2	Description	26	-
VIII-3	Claims	4	-
VIII-4	Abstract	1	icc-211.txt
VIII-5	Drawings	0	-
VIII-7	TOTAL	35	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Return Receipt Postcard	-
VIII-18	**Figure of the drawings which should accompany the abstract**		
VIII-19	**Language of filing of the international application**	English	
IX-1	**Signature of applicant or agent**		
IX-1-1	Name (LAST, First)	BAUMAN, Steven, C.	

FOR RECEIVING OFFICE USE ONLY

10-1	**Date of actual receipt of the purported international application**	
10-2	**Drawings:**	
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	ISA/US
10-6	**Transmittal of search copy delayed until search fee is paid**	

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FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	

ICC-211/PCT

PCT (ANNEX - FEE CALCULATION SHEET)

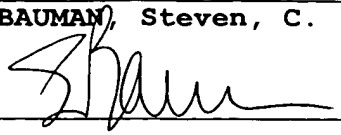
Original (for **SUBMISSION**) - printed on 07.09.2000 01:22:07 PM

(This sheet is not part of and does not count as a sheet of the international application)

0	**For receiving Office use only**			
0-1	International Application No.			
0-2	Date stamp of the receiving Office			
0-4	**Form - PCT/RO/101 (Annex) PCT Fee Calculation Sheet**			
0-4-1	Prepared using	PCT-EASY Version 2.90 (updated 08.03.2000)		
0-9	**Applicant's or agent's file reference**	ICC-211/PCT		
2	**Applicant**	LOCTITE CORPORATION, et al.		
12	**Calculation of prescribed fees**	fee amount/multiplier	total amounts (USD)	
12-1	Transmittal fee T	⇨	240	
12-2	Search fee S	⇨	700	
12-3	International fee Basic fee (first 30 sheets) b1	427		
12-4	Remaining sheets	5		
12-5	Additional amount (X)	10		
12-6	Total additional amount b2	50		
12-7	b1 + b2 = B	477		
12-8	Designation fees Number of designations contained in international application	85		
12-9	Number of designation fees payable (maximum 8)	8		
12-10	Amount of designation fee (X)	92		
12-11	Total designation fees D	736		
12-12	PCT-EASY fee reduction R	-132		
12-13	Total International fee (B+D-R) I	⇨	1,081	
12-17	**TOTAL FEES PAYABLE (T+S+I+P)**	⇨	2,021	
12-19	**Mode of payment**	authorization to charge deposit account		
12-20	**Deposit account instructions** The receiving Office:	United States Patent and Trademark Office (USPTO) (RO/US)		
12-20-1	is hereby authorized to charge the total fees indicated above to my deposit account	✓		
12-20-2	is hereby authorized to charge any deficiency or credit any over-payment in the total fees indicated above to my deposit account	✓		
12-20-3	is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account	✓		
12-21	Deposit account No.	12-2135		
12-22	Date	07 September 2000 (07.09.2000)		

PCT (ANNEX - FEE CALCULATION SHEET) ICC-211/PCT

Original (for **SUBMISSION**) - printed on 07.09.2000 01:22:07 PM

12-23	Name and signature	BAUMAN, Steven, C. 

VALIDATION LOG AND REMARKS

13-2-6	Validation messages Contents	Yellow! The power of attorney or a copy of the general power of attorney will need to be furnished unless all applicants sign the request form.
		Green? The international application contains no drawings. Please verify.
		Green? Priority 1. The priority document is not enclosed. (The applicant must furnish it within 16 months from the earliest priority date claimed)
13-2-7	Validation messages Fees	Green? Please confirm that fee schedule utilized is the latest available
13-2-8	Validation messages Payment	Green? Please ensure that you have a valid deposit account with the receiving Office selected.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

REVISED VERSION

(19) World Intellectual Property Organization
International Bureau

(10) International Publication Number
WO 01/18068 A1

(43) International Publication Date
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(54) Title: RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

(57) Abstract: A radiation-curable composition that includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component, and a photoinitiator component is provided.

VERSION

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) :C08F 2/50, 236/12, 2/50, 4/42; C09J 7/04, 4/04
US CL : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,139,388 A [REICH et al] 13 February 1979, abstract, col.2, lines 47-57, Example 1, claims 1,2.	1-4, 12/5-9, 14-18
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Y		1-4, 12/5-9, 14-18
Y	US 5,922,783 A [WOJCIAK] 13 July 1999, abstract, col.3, lines 14-21, 54-64, col.4, lines 41-67, col.5, lines 1-24, 42-45, 53-60, col.6, lines 2220-34, 42-50, col.7, 43-53, Example 1.	1-19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,530,037 A [MCDONELL et al] 25 June 1996, abstract, col.3, lines 60-66, col.4, 5, col.7, lines 14-16, Example 1, claims 1-3, 7, 11, 16, 17.	1-5, 7, 12, 14-18/6, 8-11, 13, 19 ---------- 1-5, 7, 12, 14-18/6, 8-11, 13, 19
A	EP 0 274 595 A (GENERAL ELECTRIC COMPANY) 20 July 1988, entire document.	1-19
A --- Y	US 3,940,362 A [OVERHULTS] 24 February 1976, abstract, col.2, lines 42-45, col.3, lines 15-18, 44-50, col.4, lines 55-60, col.5, lines 10-20, Examples I-XXVI, claims 1-9, 19, 21.	1-19 ----- 1-19
A	US 5,824,180 A [MIKUNI et al] 20 October 1998, entire document	1-19
A --- Y	EP 0 769 721 A (THREE BOND CO., LTD) 23 April 1997, abstract, page 3, page 10, 19-59, page 11, lines 1-5, 40-46, page 12, Table 1.	1-19 ------ 1-19

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RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to radiation-curable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component.

Brief Description of Related Technology

Cyanoacrylates generally are quick setting materials which cure to clear, hard glassy resins, useful as sealants, coatings, and particularly adhesives for bonding together a variety of substrates [see e.g., H.V. Coover, D.W. Dreifus and J.T. O'Connor, "Cyanoacrylate Adhesives" in Handbook of Adhesives, 27, 463-77, I. Skeist, ed., Van Nostrand Reinhold, New York, 3rd ed. (1990)].

Ordinarily, upon contact with substrate materials possessing a surface nucleophile, cyanoacrylate-containing compositions spontaneously polymerize to form a cured material. The cured material exhibits excellent adhesive properties to materials such as metals, plastics, elastomers, fabrics, woods, ceramics and the like.

Cyanoacrylate-containing compositions are thus seen as a versatile class of single-component, ambient temperature curing adhesives.

With conventional polymerizable compositions other than those containing cyanoacrylate monomers, radiation cure generally presents certain advantages over other known cure methods. Those advantages include reduced cure time, solvent elimination (which thereby reduces environmental pollution, and conserves raw materials and energy) and inducement of low thermal stressing of substrate material. Also, room temperature radiation cure prevents degradation of certain heat sensitive polymers, which may occur during a thermal cure procedure.

Radiation-curable, resin-based compositions are legion for a variety of uses in diverse industries, such as coatings, printing, electronic, medical and general engineering. Commonly, radiation-curable compositions are used for adhesives, and certain of the compositions are acrylate-based compositions.

Well-known examples of radiation-curable, acrylate-based resins include those having structural backbones of urethanes, amides, imides, ethers, hydrocarbons, esters and siloxanes. [See e.g., J.G. Woods, "Radiation-Curable Adhesives" in Radiation Curing: Science and Technology, 333-98, 371, S.P. Pappas, ed., Plenum Press, New York (1992).] The common cure mechanism for such radiation-curable, acrylate-based compositions is reported to be free-radical polymerization.

European Patent Publication EP 393 407 describes a radiation-curable composition which includes a slow cure cationic polymerizable epoxide, a fast cure free radical polymerizable acrylic component and a photoinitiator. Upon exposure to radiation, the photoinitiator is said to be capable of generating a cationic species which is capable of initiating polymerization of the epoxide and a free radical species which is capable of initiating polymerization of the acrylic component. The polymerizable acrylic component

includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters, examples of which are expressed as 2-cyanoethyl acrylate (CH_2=CHCOOCH_2CH_2CN) and 3-cyanopropyl acrylate (CH_2=CHCOO$CH_2CH_2CH_2$CN). (See page 5, lines 19-26.)

U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

In C. Kutal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^-, cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Kutal) 5,691,113 (Kutal) and 5,877,230 (Kutal).

International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α-cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VII of the periodic table and aromatic electron system ligands selected from π-arenes, indenyl, and η-cyclopentadienyl. The photocurable composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni)

describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition component would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism, thereby providing to the compositions (and cured reaction products formed therefrom) the benefits and advantages of curing through such a mechanism. More specifically, photocurable compositions of this invention cure rapidly when used, and in so doing minimize the opportunity for undesirable blooming or crazing formation in the cured reaction product. In addition, the inventive photocurable compositions are capable of curing through larger gaps between substrate surfaces than conventional cyanoacrylates, or known photocurable cyanoacrylates. Moreover, as set forth in greater detail below, in one aspect of the invention the photocurable compositions include a non-cyanoacrylate-based radical curable component. The precense of such a component in the inventive compositions allows for the generation of copolymers and reaction products, which would not otherwise be accesible through typical anionic polymerization mechsanisms -- the predominant polymerization of cyanoacrylates.

In another aspect of the present invention, there is provided a method of polymerizing a photocurable composition by providing an amount of the composition to a desired surface and exposing the composition to radiation in an amount sufficient to effect cure thereof.

In yet another aspect of the present invention, there is provided the cured reaction product formed from a photocurable composition after exposure thereof to a curingly effective amount of radiation.

The present invention will be more readily appreciated by those persons of skill in the art based on a reading of the detailed description of the invention which follows and the examples presented thereafter for illustrative purposes.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to photocurable compositions, which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoiniated radical generating component and a photoinitiator component.

The cyanoacrylate component or cyanoacrylate-containing formulation includes cyanoacrylate monomers which may be chosen with a raft of substituents, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, such as n-propyl- or i-propyl-2-cyanoacrylate, butyl-2-cyanoacrylates, such as n-butyl- or i-butyl-2-cyanoacyrlate, octyl-2-cyanoacrylates, such as n-alkyl-, 2-alkyl-2-cyanoacrylate, and the like, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable cyanoacrylate monomer for use herein is ethyl-2-cyanoacrylate.

Among the different types of materials appropriate for use as the photoiniated radical generating component desirable ones share at least these common features: they possess electron withdrawing substituents present at at least one portion of the molecule, thereby rendering the portion(s) electron deficient. And when placed in contact with a photoexcitable material (such as a dye), which when exposed to radiation of an appropriate wavelength, absorbs energy sufficient to cause the radical initiator to cleave at the electron deficient portion(s) of the molecule, thereby generating free radicals.

A variety of photoiniated radical generating components are suitable for use herein, such as α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, and peresters. Of course, combinations of these compounds may also be used.

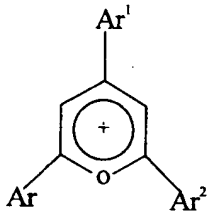
More specific examples of such materials include azoisobutyronitrile ("AIBN"), 1,1'-azo-bis(cyclohexane carbonitrile) ("ABCH"), 4,4'-azo-bis(4-cyanovaleric acid) ("ABCV"), 1,1'-(azodicarbonyl)-dipiperidine ("ADCDP"), 1,1-bis(t-butylperoxy)cyclohexane ("BBPH"), 2,5-bis(t-butylperoxy)2,5-dimethylhexane ("BBPDMH"), bis[1-(t-butylperoxy)-1-methyl-ethyl]benzene ("BBPMEB"), benzoin methylether ("BME"), cumylhydroperoxide ("CHPO"), dibenzoylperoxide ("DBPO"), di-t-butylperoxide ("DTBPO"), 2,2-diethoxyacetophenone ("DEAP"), 2,2-dimethoxy-phenylacetophenone ("DMPAP"), dicumylperoxide ("DCPO"), diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide ("DPTPO"), desylchloride ("DC"), lauroylperoxide ("LPO"), t-butylperoxybenzoate ("TBPB"), and t-butylhydroperoxide ("TBHPO").

Other examples include those available commercially from Ciba Specialty Chemicals Corp., Tarrytown, New York under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl) phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one), and 819 [bis(2,4,6-trimethyl benzoyl) phenyl phosphine oxide] and "DAROCUR" 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and 4265 (the combination of 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one); and the visible light [blue] photoinitiators, dl-camphorquinone and "IRGACURE" 784DC (bis(η^5-2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium).

Of course, combinations of these materials may also be employed herein.

Photoinitiators enhance the rapidity of the curing process when the radiation compositions are exposed to electromagnetic radiation. A number of photoinitiators may be employed herein, examples of which include, but are not limited to,

Photoinitiators useful herein include pyrylium-based materials having a core structure of



X^-

where each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion, such as halogen, hexahalophosphate, hexahaloarsenate, hexahaloantimonate, tetrahaloferrate, tetrahaloborate (e.g., fluoro, chloro, bromo and iodo), and sulfonate.

More specific representations of the pyrylium-based materials include: 2,4,6-triphenylpyrylium-tetrafluoroborate ("TPT"), 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium-tetrafluoroborate) ("PBT"), 2,4-diphenylnaphto-(1,2-B) pyrylium-tetrafluoroborate ("DNT"), 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate ("TPTS"), and 2,6-dipenyl-4(p-tolyl)-pyrylium tetrafluoroborate ("DTPT").

In the aspect of the invention where a non-cyanoacrylate-based radical curable component is included in the inventive compositions, such radical curable component may be selected from a wide variety of materials, such as alkenes or alkynes.

Of these, styrene and derivatives thereof, such as alkyl- and alkenyl-ether derivatives, (meth)acrylates, alkyl- and aryl or alkenyl acetylenes, as well as esters of vinyl alcohol (e.g., vinyl acetate), are particularly desirable.

With respect to formulating photocurable compositions, generally the components may be introduced to one another in any convenient order. Alternatively, it may be desirable to prepare a premix of the radical initiator component and the photoinitiator component. In this way, a ready made premix of those components may be added to the cyanoacrylate component of the formulation to allow for a quick and easy one-part formulation of a photocurable composition prior to dispensing and curing thereof.

For packaging and dispensing purposes, it may be desirable for photocurable compositions in accordance with the present invention to be relatively fluid and flowable. Variations in the viscosity thereof may also be desirable in certain applications and may be readily achieved through routine changes in formulation, the precise changes being left to those persons of ordinary skill in the art.

For instance, ordinarily cyanoacrylate-containing compositions free from an added thickener or viscosity modifier are low viscosity formulations (such as in the range of 1 to 3 cps). While a composition with such a viscosity (or one whose viscosity has been modified to be up to about five times that viscosity) may be appropriate for a wicking application where a small gap exists between sustrates to be bound (e.g., less than about 0.1 mils) and/or an application where enhanced cure speed is desirable, such a viscosity may be too low for convenient use in certain industrial applications. At least for this reason, the viscosity of cyanoacrylate-containing compositions has at times been desirably modified through, for instance, the addition of polymethylmethacrylates and/or fumed silicas. See e.g., U.S. Patent Nos. 4,533,422 (Litke) and Re. 32,889 (Litke), the disclosures of each of which are hereby expressly incorporated herein by reference.

A medium viscosity formulation (such as in the range of 100 to 300 cps) may be more appropriate in applications where greater control of flowability is desirable. And a high viscosity formulation (such as in the

range of 600 to 1000 cps) may be more appropriate in applications involving porous substrates and/or substrates with larger gaps (such as greater than about 0.5 mils).

Of course, those persons of skill in the art should make appropriate decisions regarding whether a viscosity modifier should be included in the photocurable composition, and if so which one(s) and at what level should one be included to achieve the desired viscosity for the intended applications.

In addition, it may be desirable to toughen the cured photocurable compositions of the present invention through the addition of elastomeric rubbers such as is taught by and claimed in U.S. Patent No. 4,440,910 (O'Connor), the disclosure of which is hereby expressly incorporated herein by reference. It may also be desirable to improve the hot strength of the cured photocurable compositions by addition of anhydrides, such as is taught by and claimed in U.S. Patent No. 4,450,265 (Harris) and the documents cited therein, the disclosures of each of which are hereby expressly incorporated herein by reference.

Moreover, the compositions of the present invention may be rendered into a thixotropic paste through addition of powdered organic fillers having a particle size of about 2 to 200 microns as is taught by U.S. Patent No. 4,105,715 (Gleave) or thickened by a copolymer or terpolymer resin to improve peel strength as is taught by U.S. Patent No. 4,102,945 (Gleave), the disclosures of each of which are hereby incorporated herein by reference.

Further, the compositions of the present invention may be rendered more resistant to thermal degradation at elevated temperature conditions by the inclusion of certain sulfur-containing compounds, such as sulfonates, sulfinates, sulfates, sultones and sulfites as set forth in U.S. Patent No. 5,328,944 (Attarwala), the disclosure of which is hereby expressly incorporated herein by reference. The inclusion of such compounds in the photocurable compositions of the present invention renders those compositions well-suited for

applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a phtotiniated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α-halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phospine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or

ketocoumarine derivatives, in an amount within the range of about 0.5% to about 10% by weight of the composition, with about 2% to about 4% or greater by weight of the total composition being desirable. The balance of the composition is composed predominantly of a cyanoacrylate component, such as ethyl-2-cyanoacrylate. Of course, the amount of all the components -- including stabilizers -- together in the composition totals 100%.

A method of curing a photocurable composition in accordance with this invention is also provided herein, the steps of which include (a) providing onto a desired surface an amount of a photocurable composition; and (b) subjecting the composition to radiation sufficient to effect cure thereof.

The amount of photocurable composition provided should be sufficient to cure and form an adequate bond to the substrate surfaces between which it is applied. For instance, application of the photocurable composition may be achieved by dispensing the composition in drop-wise fashion, or as a liquid stream, brush-applied, dipping, and the like, to form a thin film. Application of the photocurable composition may depend on the flowability or viscosity of the composition. To that end, viscosity modifiers, as noted above, may be included in the composition.

The photocurable compositions of the present invention have taken the ordinary undesirable by-product free radical reaction that compromises shelf life stability and turned it into a controlled free radical cure mechanism.

In use, such compositions are desirably readily dispensed onto a portion of a desired surface of a substrate onto which is to be bonded a portion of another substrate. The photocurable composition may be applied to certain portions of the substrate surface or over the entire surface of the substrate to be bonded, depending on the particular application.

The source of radiation emitting electromagnetic waves is selected from ultraviolet light, visible light,

electron beam, x-rays, infrared radiation and combinations thereof. Desirably, ultraviolet light is the radiation of choice, with appropriate sources including "H", "D", "V", "X", "M" and "A" lamps, mercury arc lamps, and xenon arc lamps (such as those commercially available from Loctite Corporation, Rocky Hill, Connecticut; Fusion UV Curing Systems, Buffalo Grove, Illinois; Spectroline, Westbury, New York; or Xenon Corp., Woburn, Massachusetts; microwave-generated ultraviolet radiation; solar power and fluorescent light sources. Any of these electromagnetic radiation sources may use in conjunction therewith reflectors and/or filters, so as to focus the emitted radiation onto a specific portion of a substrate onto which has been dispensed a photocurable composition and/or within a particular region of the electromagnetic spectrum. Similarly, the electromagnetic radiation may be generated directly in a steady fashion or in an intermittent fashion so as to minimize the degree of heat build-up. Although the electromagnetic radiation employed to cure the photocurable compositions into desired reaction products is often referred to herein as being in the ultraviolet region, that is not to say that radiation in other regions within the electromagnetic spectrum may not also be suitable. For instance, in certain situations, radiation in the visible region of the electromagnetic spectrum may also be advantageously employed, whether alone or in combination with, for instance, radiation in the ultraviolet region. Of course, microwave and infrared radiation may also be advantageously employed under appropriate conditions.

Higher or lower radiation intensities, greater or fewer exposures thereto and length of exposure and/or greater or lesser distances of the source of radiation to the composition may be required to complete curing, depending of course on the particular components of a chosen composition.

More specifically with respect to radiation intensity, the chosen lamp should have a power rating of at

least about 100 watts per inch (about 40 watts per cm), with a power rating of at least about 300 watts per inch (about 120 watts per cm) being particularly desirable. Also, since the inclusion of a photoinitiator in the composition may shift the wavelength within the electromagnetic radiation spectrum at which cure occurs, it may be desirable to use a source of electromagnetic radiation whose variables (e.g., wavelength, distance, and the like) are readily adjustable.

During the curing process, the composition will be exposed to a source of electromagnetic radiation that emits an amount of energy, measured in mW/cm^2, determined by parameters including: the size, type and geometry of the source; the duration of the exposure to electromagnetic radiation; the intensity of the radiation (and that portion of radiation emitted within the region appropriate to effect curing); the absorbency of electromagnetic radiation by any intervening materials, such as substrates; and the distance the composition lies from the source of radiation. Those persons of skill in the art should readily appreciate that curing of the composition may be optimized by choosing appropriate values for these parameters in view of the particular components of the composition.

To effect cure, the source of electromagnetic radiation may remain stationary while the composition passes through its path. Alternatively, a substrate coated with the photocurable composition may remain stationary while the source of electromagnetic radiation passes thereover or therearound to complete the transformation from composition to reaction product. Still alternatively, both may traverse one another, or for that matter remain stationary, provided that the photocurable composition is exposed to electromagnetic radiation sufficient to effect cure.

Commercially available curing systems, such as the "ZETA" 7200 or 7400 ultraviolet curing chamber (Loctite Corporation, Rocky Hill, Connecticut), "UVALOC" 1000 (Loctite Deutschland GmbH, Münich, Germany), Fusion UV Curing Systems F-300 B (Fusion UV Curing Systems, Buffalo

Grove, Illinois), Hanovia UV Curing System (Hanovia Corp., Newark, New Jersey), BlackLight Model B-100 (Spectroline, Westbury, New York), and RC500 A Pulsed UV Curing System (Xenon Corp., Woburn, Massachusetts), are well-suited for the purposes described herein. Also, a Sunlighter UV chamber fitted with low intensity mercury vapor lamps and a turntable may be employed herein.

The required amount of energy may be delivered by exposing the composition to a less powerful intensity of electromagnetic radiation for a longer period of time, through for example multiple passes, or alternatively, by exposing the composition to a more powerful intensity of electromagnetic radiation for a shorter period of time. In addition, each of those multiple passes may occur with an intensity at different energy intensities. In any event, those persons of skill in the art should choose an appropriate intensity of electromagnetic radiation depending on the particular composition, and position the source of electronic radiation at a suitable distance therefrom which, together with the length of exposure, optimizes transformation. Also, it may be desirable to use a source of electromagnetic radiation that is delivered in an intermittent fashion, such as by pulsing or strobing, so as to ensure a thorough and complete cure without causing excessive heat build-up.

In use, a photocurable composition in accordance with the present invention may be dispensed, such as in the form of a thin film or droplet, onto a desired substrate. Substrates onto which the photocurable composition of the present invention may be applied may be chosen from a vast selection of different materials; basically, any material with which cyanoacrylates may be used is suitable as well for use herein. See supra.

Desirable choices among such materials include acrylics, epoxies, polyolefins, polycarbonates, polysulfones (e.g., polyether sulfone), polyvinyl acetates, polyamides, polyetherimides, polyimides and derivatives and co-polymers

thereof with which may be blended or compounded traditional additives for aiding processibility or modifying the physical properties and characteristics of the material to be used as a substrate. Examples of co-polymers which may be employed as substrates include acrylonitrile-butadiene-styrene, styrene-acrylonitrile cellulose, aromatic copolyesters based on terephthallic acid, *p,p*-dihydroxybiphenyl and *p*-hydroxy benzoic acid, polyalkylene (such as polybutylene or polyethylene) terephthalate, polymethyl pentene, polyphenylene oxide or sulfide, polystyrene, polyurethane, polyvinylchloride, and the like. Of course, other materials may also be employed for use herein. Particularly, desirable co-polymers include those which are capable of transmitting UV and/or visible radiation.

The composition-coated substrate may be positioned within an electromagnetic radiation curing apparatus, such as the "ZETA" 7200 ultraviolet curing chamber or the "UVALOC" 1000 ultraviolet curing chamber, equipped with an appropriate source of electromagnetic radiation, such as ultraviolet radiation, at an appropriate distance therefrom, such as within the range of about 1 to 2 inches, with about 3 inches being desirable. As noted above, the composition-coated substrate may remain in position or may be passed thereunder at an appropriate rate, such as within the range of about 1 to about 60 seconds per foot, with about 5 seconds per foot. Such passage may occur one or more times, or as needed to effect cure of the composition on the substrate. The length of exposure may be in the range of a few seconds or less (for one time exposure) to tens of seconds or longer (for either a one time exposure or a multiple pass exposure) if desired, depending on the depth of the composition to be cured and of course on the components of the composition themselves.

A reaction product is also of course provided by the teaching of this invention. The reaction product is formed from photocurable compositions after exposure thereof

to electromagnetic radiation sufficient to effect cure of the composition. The reaction product is formed rapidly, and ordinarily and desirably without observed formation of blooming or crazing, see infra.

The reaction product of the photocurable composition may be prepared by dispensing in low viscosity or liquid form a photocurable composition in accordance with present invention onto a substrate and mating that substrate with a second substrate to form an assembly. Thereafter, exposure to electromagnetic radiation on at least one substrate of the assembly for an appropriate period of time should transform the photocurable composition into an adhesive reaction product.

It is also within the scope of the present invention for reaction products to be prepared from a photocurable composition separately from the device, and thereafter positioned on a substrate surface with which it is to be used.

The viscosity of the photocurable composition may be controlled or modified to optimize its dispensability by, in addition to inclusion of an appropriate material to alter the viscosity thereof as noted above, adjusting the temperature of (1) the composition itself, or (2) the substrates on which the composition may be placed to assemble the device. For example, the temperature of the composition or the substrate(s) or combinations thereof may be decreased to increase the viscosity of the composition. In this way, the uniformity on the substrate of the dispensed photocurable composition may be enhanced using lamination techniques, centrifuge techniques, pressure applied from the atmosphere (such as with vacuum bagging), pressure applied from a weighted object, rollers and the like.

The substrates onto which the photocurable compositions of the present invention are intended to be dispensed may be constructed from the litany of materials recited supra, which may be substantially inflexible as well

as flexible. The type of substrate chosen with respect to flexibility will of course depend on the application for which it is to be used. More specifically, the substrates may be constructed from substantially inflexible materials, such as glass, laminated glass, tempered glass, optical plastics, such as polycarbonates, acrylics and polystyrenes, and other alternatives as noted supra; and flexible materials, such as "MYLAR" film or polyolefin, such as polyethylene or polypropylene, tubing.

The choice of substrate material may influence the choice of processing technique used to prepare the photocurable composition into the cured reaction product or the type of device assembled. For example, when assembling a device from at least one flexible substrate, a composition may be advantageously applied to an end portion of the flexible substrate and allowed to wick along that end portion through a portion of another substrate, which is dimensioned to receive that end portion of the flexible substrate. A particular example of such an application is polyolefin tubing intended for medical applications, one end portion of which is dimensioned for receiving by an acrylic luer housing.

Since the photocurable compositions of the present invention cure to form reaction products through a photo-initiated free radical mechanism, the composition is exposed to the source of electromagnetic radiation to effect cure. The choice of substrate may affect the rate and degree at which cure occurs of the photocurable compositions of the present invention. For instance, it is desirable for the substrates to be bonded together to be substantially free of electromagnetic radiation-absorbing capabilities. That is, the greater degree of electromagnetic radiation transmitting capability the substrate possesses, the greater the rate and degree of cure of the composition, all else being equal of course.

It may be desirable to package the inventive compositions in a two part package, particularly in those

instances where a cyanoacrylate component and a non-cyanoacrylate radical curable component are present.

Blooming or crazing may be observed when compositions cure into reaction products and the cure itself is incomplete. That is, blooming refers to the evaporation of cyanoacrylate monomer (due to its relatively high vapor pressure) from uncured fillets, the result of which is formation of a precipitate on surfaces adjacent to the bond line which are also observed as a white haze. Crazing refers to the formation of stress cracks on certain synthetic materials, such as polycarbonates, acrylics and polysulfones, due in this instance to the presence thereon of cyanoacrylate monomer.

The result of incomplete curing may be observed with respect to adhesive uses of the photocurable composition as adhesive or cohesive failure of the cured composition when applied to or between substrates. Such observations may be minimized or even eliminated by using electromagnetic radiation transmitting (as contrasted to absorbing) substrates and placing the source of electromagnetic radiation at a strategic location so as to improve the degree of electromagnetic radiation to which the composition on the substrate is exposed. Similarly, additional sources of electromagnetic radiation, or as stated above reflectors which redirect onto desired portions of the substrate stray or errant electromagnetic radiation, may be employed to further enhance cure.

The compositions of the present invention minimize and often eliminate blooming and crazing in commercial applications of the compositions by curing through the photoinitiated mechanism.

In addition, the compositions of this invention provide a built-in secondary cure system (i.e., photo-initiated free radical initial in addition to the ordinary cyanoacrylate anionic initiation), which is particularly attractive in those applications where certain of the substrates which may be used in the assembly do not allow

the transmission of light, rendering another type of adhesive (such as a dual cure acrylic adhesive) less desirable because a secondary heating step would then be required; elimination of a substrate primer step, which obviates the use of often flammable materials and invites automated processes; and improved cure through volume capabilities.

In view of the above description of the present invention, it is evident that a wide range of practical opportunities is provided by the teaching herein. Certain of those practical opportunities are exemplified below, as are many of the advantages and benefits of the present invention. However, the invention as so exemplified is for illustrative purposes only and is not to be construed in any way as limiting the broad aspects of the teaching herein provided.

EXAMPLES

Example 1

In this example, formulations were prepared to demonstrate the effect of one or the other of a radical initiator component and a photoinitiator component in ether to cyanoacrylate composition. The photoinitiated radical generating component chosen was dibenzoyl peroxide ("DBPO") and the photoinitiator component was 2,4,6-triphenylpyrylium tetraflouroborate ("TPT"). The formulations were prepared by mixing the appropriate components with the cyanoacrylate and thereafter dispensing a drop of the formulation onto a polycarbonate slide. The slide was then exposed to 1000 watts of mercury arc light in a "UVALOC" 1000 irradiation chamber for a period of time of about 30 seconds. The results of this example are shown below in Table 1.

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinititor component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that
vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained

in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of mercury arc light and/or when one drop of the sample was placed on a glass slide and a second glass slide was positioned thereover, and thereafter exposing the single or double glass slide assembly to a Philips lamp HPR125 at 6 mW/cm^2 intensity or to no extra light at all.

Table 2

Sample No.	TPT [ppm]	Radical Initiator		Curing Speed [secs]		
				1000 W 1 glass slide	2 glass slides	
		Type	[ppm]		6 mW/cm^2	No light
14	2000	DBPO	100	29	2	>50
15	2000	DBPO	150	28	2	>50
16	2000	DBPO	250	29	2	>50
17	2000	DBPO	350	31	1-2	>50
18	2000	DBPO	450	31	1-2	>50
19	2000	DBPO	600	34	1-2	>50
20	2000	DBPO	1000	35		
21	2000	DBPO	5000	35		
22	2000	TBPB	600	35		
23	2000	TBPB	1000	35		
24	2000	TBPB	5000	35		
25	2000	DTBPO	400	35		
26	2000	DTBPO	1000	35		
27	2000	DTBPO	5000	35		
28	2000	DEAP	200	40		
29	2000	DEAP	1000	30		
30	2000	DEAP	5000	35		
31	2000	DMPAP	200	35		
32	2000	DMPAP	1000	30		
33	2000	DMPAP	5000	30		
34	2000	ABCH	400	33		
35	2000	ABCH	2000	40		
36	2000	BBPH	400	40		
37	2000	AIBN	100	31	1	>50
38	2000	AIBN	200	31	1-2	>50
39	2000	AIBN	400	29	1-2	>50
40	2000	AIBN	800	30	1-2	>50
41	2000	AIBN	2000	30	2	>50
42	2000	AIBN	4000	31	2-3	>50
43	4000	AIBN	2000	33		
44	4000	AIBN	4000	35		
45	2000	DCPO	200	40		
46	2000	DCPO	1000	35		
47	2000	DCPO	5000	40		
48	2000	ABCV	400	55		
49	2000	ABCV	2000	55		

50	2000	TBHPO	400	50		
51	2000	TBHPO	2000	45		
52	2000	BBPDMH	400	38		
53	2000	BBPDMH	2000	38		
54	2000	BBPDMH	400	35		
55	2000	BBPDMH	2000	40		
56	2000	ADCDP	400	22		
57	2000	ADCDP	2000	15		
58	2000	LPO	400	30		
59	2000	LPO	2000	32		
60	2000	DPTPO	400	35		
61	2000	DPTPO	2000	22		
62	2000	DC	400	45		
63	2000	DC	2000	55		
64	2000	CHPO	400	50		

Table 2 shows that a variety of photoinitiated radical generating components may be used to render a cyanoacrylate-containing formulation photocurable in the presence of a photoinitiator -- in this case TPT. Such photoinitiated radical generating components include, in addition to DBPO, other peroxides, peresters, azo-compounds, halo acetophenones (e.g., DC), aromatic carbonyl compounds (e.g., DMPAP and DEAP), acyl phosphine oxides (e.g., DPTPO) and related compounds.

Example 3

In this example, a variety of different photoinitiator components were chosen for evaluation in an ethyl-2-cyanoacrylate formulation with DBPO as a phtoinitiated radical generating component, with one exception being AIBN in Sample No. 74. The specific photoinitiator components chosen and the amounts used are set forth below in Table 3, as well are the curing speeds of the formulations.

Table 3

Sample No.	Radical Initiator		Photoinitiator		Curing Speed [secs]		
					1000 W 1 slide glass	2 glass slides	
	Type	[ppm]	Type	[ppm]		6 mW/cm^2	No light
65	DBPO	100	TPT	2000	29	2	>50
66	DBPO	150	TPT	2000	28	2	>50
67	DBPO	250	TPT	2000	29	2	>50
68	DBPO	350	TPT	2000	31	1-2	>50
69	DBPO	200	PBT	2000		25	>50
70	DBPO	200	DNT	2000		1	10
71	DBPO	200	DNT	5000	45	1-2	40
72	DBPO	200	TPTS	2000		4	45
73	DBPO	200	TPTS	5000	40	2	>50
74	AIBN	500	DTPT	2000	30	2	>50
75	DBPO	250	DTPT	2000	35	2	>50
76	DBPO	250			>60	>30	>30
77	DBPO	200	CPPP	2000	>50		
78	DBPO	200	CPPP	3000	>50	>50	>50
79	DBPO	200	DMPT	2000	>50	>50	
80	DBPO	200	DMPPC	2000		35	
81	DBPO	200	DMPPC	5000	40	20	20
82	DBPO	200	BHNT	2000		>50	
83	DBPO	200	BHNT	3000	40	45	
84	DBPO	200	DFPT	2000		>50	
85	DBPO	200	DFPT	5000	40	>50	
86	DBPO	250	CBMOC	2000	>60	>50	>50
87	DBPO	250	ADCN	2000	>60	>50	>50

Example 4

In this example, a side-by-side evaluation of a cyanoacrylate composition (one with TPT at a 2000 ppm level and DBPO at a 200 ppm level) curing in the presence of air and in the presence of a nitrogen atmosphere demonstrated that the presence of oxygen inhibits the ability of the composition to cure.

In addition, cyanoacrylate compositions with TPT as a photoinitiator component at 1500 ppm and varied levels of DBPO as a radical initiator component, where the amount was varied, were cured to illustrate that these compositions cure through a free radical initiated mechanism.

In Table 4a below, the effect is shown of increasing the level of DBPO on the cure speed of a composition (Sample No. 65) on a polycarbonate slide when exposed to mercury arc light at an intensity of 1000 W.

Increasing the level of DBPO shows an increase in the time required to achieve a tack free surface from the formulation.

An optimum concentration for the photoinitiated radical generating component may indicate the radical nature of the photocuring effect. That is, at a low concentration, the decay of the photoinitiated radical generating component, e.g., DBPO, triggers the growth of macroradicals; at a higher concentration a part of the DBPO may also quench chain propagation.

Table 4a

DBPO [ppm]	Cure speed @ 1000 W [secs]
100	30
200	25
300	20
400	30
800	45

In Table 4b below, a composition within the scope of this invention (Sample No. 88) was prepared and evaluated for tack free time. A composition having the same radical initiator component and the same photoinitiator component in the same amounts (Sample No. 89) was also prepared, to which was added 2000 ppm of hydroquinone. Hydroquione is a known free radical scavenger. In the table it may be seen that the introduction of the hdroquinone vastly retards, if not completely impedes within a reasonable time period, the ability of the composition to cure when exposed to UV light. This data indicates that the inventive compositions cure through a radical initiated mechanism.

Table 4b

Sample No.	DBPO [ppm]	TPT [ppm]	Tack-free time @ 1000 W [secs]
88	200	2000	26
89	200	2000	>60

Example 5

In this example, a non-cyanoacrylate radical curable component was included with the cyanoacrylate to illustrate the ability of the so-formed formulations to cure when exposed to appropriate radiation in the electromagnetic spectrum. The identity of such components, the percent by weight added and the speed of cure are set forth below in Table 5.

Table 5

Sample No.	Non-Cyanoacrylate Radical Curable Component		Curing speed [secs]
	Type	Amt[%]	
90	--	--	6
91	Styrene	25	6
92	Styrene	50	8
93	Styrene	75	16
94	Tetrahydrofurfuryl methacrylate	25	40
95	Tetrahydrofurfuryl methacrylate	50	32
96	Isodecyl methacrylate	25	15
97	Phenylacetylene	50	18
98	2-Phenylethyl methacrylate	50	34
99	Trimethylphenyl acrylate	50	36
100	Pentaerythritol tetraacrylate	50	12

Example 6

In this example, a variety of photoinitiated radical generating components were added to ethyl-2-cyanoacrylate in various amounts, with and without 2500 ppm of TPT as a photoinitiator, to determine the cure speed after exposure to UV light at an intensity of 1000 W in an irradiation chamber ("UVALOC 1000", Loctite Deutschland GmbH).

More specifically, Sample Nos. 102, 104, 106, 108, 110, 112, 114, 116, 118, and 120 contained TPT.

Table 6

Sample No.	Photoinitiated Radical Generating Component					Curing Time [secs]
	AIBN	LUCIRIN TPO	IRGACURE 184	IRGACURE 651	IRGACURE 907	
101	500					>60
102	500					34
103	20000					*
104	20000					42
105		1500				*
106		1500				26
107		20000				*
108		20000				13
109			1500			*
110			1500			45
111			20000			*
112			20000			>60
113				1500		*
114				1500		50
115				20000		*
116				20000		>60
117					1500	>60
118					1500	4
119					20000	15
120					20000	3

* No curing observed; sample evaporates before curing.

While the present invention has been exemplified as shown above, it is clear that variations are also intended to be within the spirit and scope of the present invention and may be practiced in accordance herewith, with only routine, rather than undue, experimentation. Any variations and equivalents should provide suitable, if not comparable results, when viewed in connection with the results obtained from the above examples. Accordingly, such variations and equivalents are also intended to be encompassed by the claims.

What Is Claimed Is:

1. A photocurable composition comprising:

(a) a 2-cyanoacrylate component,

(b) a photoinitiated radical generating component, and

(c) a photoinitiator component.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by $H_2C=C(CN)-COOR$, wherein R is selected from the group consisting of C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

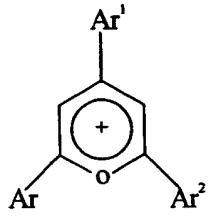
5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclohexane, 2,5-bis(t-butylperoxy)-2,4-

dimethylhexane, bis[1-(t-butylperoxy)-1-methyl-ethyl]benzene, benzoin methylether, cumylhydroperoxide, dibenzoylperoxide, di-t-butylperoxide, 2,2-diethoxyacetophenone, 2,2-dimethoxy-phenylacetophenone, dicumylperoxide, diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide, desylchloride, lauroylperoxide, t-butylperoxybenzoate, t-butylhydroperoxide and combinations thereof.

7. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-, trimethyl pentyl phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-2-methyl-1-phenyl-1-propane, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

8. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of within the following structure:



X^-

wherein each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium

tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to any one of Claims 1-11, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to any one of Claims 1-11, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to any one of Claims 1-14; and

(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to any one of Claims 1-14 in a two-part formulation.

17. The composition according to any one of Claims 1-14 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to any one of Claims 1-14 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to any one of Claims 1-14, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

INTERNATIONAL SEARCH REPORT

International application No.
P[redacted]00/24620

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08F 2/50, 236/12, 2/50, 4/42; CO9D 3/80; C08J 7/04, 4/04
US CL : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0; STN CA PLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,139,388 A [REICH et al] 13 February 1979, abstract, col.2, lines 47-57, Example 1, claims 1,2.	1-4, 12/5-9, 14-18 --- 1-4, 12/5-9, 14-18
Y	US 5,922,783 A [WOJCIAK] 13 July 1999, abstract, col.3, lines 14-21, 54-64, col.4, lines 41-67, col.5, lines 1-24, 42-45, 53-60, col.6, lines 2220-34, 42-50, col.7, 43-53, Example 1.	1-19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 11 OCTOBER 2000	Date of mailing of the international search report 02 JAN 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-8819

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24620

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,530,037 A [MCDONELL et al] 25 June 1996, abstract, col.3, lines 60-66, col.4, 5, col.7, lines 14-16, Example 1, claims 1-3, 7, 11, 16, 17.	1-5, 7, 12, 14-18/6, 8-11, 13, 19 ---------- 1-5, 7, 12, 14-18/6, 8-11, 13, 19
A	EP 0 274 595 A (GENERAL ELECTRIC COMPANY) 20 July 1988, entire document.	1-19
A --- Y	US 3,940,362 A [OVERHULTS] 24 February 1976, abstract, col.2, lines 42-45, col.3, lines 15-18, 44-50, col.4, lines 55-60, col.5, lines 10-20, Examples I-XXVI, claims 1-9, 19, 21.	1-19 ----- 1-19
A	US 5,824,180 A [MIKUNI et al] 20 October 1998, entire document	1-19
A --- Y	EP 0 769 721 A (THREE BOND CO., LTD) 23 April 1997, abstract, page 3, page 10, 19-59, page 11, lines 1-5, 40-46, page 12, Table 1.	1-19 ------ 1-19

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL CT 06067

PCT

WRITTEN OPINION
(PCT Rule 66)

Date of Mailing *(day/month/year)*	26 JUL 2001
Applicant's or agent's file reference: ICC-211/PCT	**REPLY DUE** within **TWO** months from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/24620	08 SEPTEMBER 2000	09 SEPTEMBER 1999

International Patent Classification (IPC) or both national classification and IPC
Please See Supplemental Sheet.

Applicant
LOCTITE CORPORATION

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I [X] Basis of the opinion
- II [ ] Priority
- III [ ] Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV [ ] Lack of unity of invention
- V [X] Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI [ ] Certain documents cited
- VII [ ] Certain defects in the international application
- VIII [X] Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension., see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 09 JANUARY 2002.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	DEBORAH THOMAS PARALEGAL SPECIALIST TANYA ZALUKAEVA
Facsimile No. (703) 305-3230	Telephone No. (703) 308-8819

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 13-19 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims 13-19 are indefinite for the following reason(s): Multiple depenedent claim cannot depend on other multiple dependent claim(s). Accordingly claims 13-19 have not been further treated on the merits.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

TIME LIMIT:

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): C08F 2/50, 236/12, 2/50, 4/42; C09J 7/04 and US Cl.: 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
iso-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, allyl, methoxyethyl,ethoxyethyl, 3-methoxybutyl and methoxyisopropyl cyanoacrylate esters (col. 4, lines 61-67).
One of preferred antioxidants is butyl hydroxy toluene (BHT, or 4-methyl-2,6-di-tert-butylphenol
Other anti-oxidants which may be used include methyl hydroquinone, catechol, tert-butyl hydroquinone, 4-tert-butoxyphenol, 4-ethoxyphenol, 3-methoxyphenol, 2-tert-butyl-4-methoxyphenol, and 2,2-methylene-bis-(4-methyl-6-tert-butylphenol).

Anionic (acid) stabilizers for cyanoacrylate adhesives include Sulphur Dioxide, Sulphonic Acids, Sulphuric Acid, Sulphur Trioxide, Phosphorous Acids, Carboxylic Acids, Picric Acid, Boron Trifluoride, etc. (col. 5, lines 35-66, col. 6, lines 1-5.

Claims 5-9 lack an inventive step under PCT Article 33(3) as being obvious over REICH et al. REICH discloses the composition as instantly claimed, with the present of an initiator, but does not specifically disclose the nature of initiators used. However, one skilled in the art would have been reasonably motivated to utilize conventionally applicable intiators with the reasonable expectation of success.

Claims 6, 8-11 an inventive step under PCT Article 33(3) as being obvious over McDONNELL.
McDONNELL discloses a cyanoacrylate adhesives as instantly claimed, however does not disclose the same photoinitiators, as per instant claims 6, 8-11. Because the poly;ymerization of MCDONNEL takes place under gamma-irradiation, one skilled in the art would have found it obvious to introduce imitators capable of producing radicals under irradiation with very short wavelength, which are mostly the instantly claimed compounds, and thus to arrive at the instant claims.

Claims 1-9 lack an inventive step under PCT Article 33(3) as being obvious over WOJCIAK (U.S. 5,922,783).
WOJCIAK discloses radiation-curable composition which includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a metallocene component and a polymerizingly effective amount of a photoinitiator to accelerate the rate of cure (abstract).

The cyanoacrylate monomer is selected from methyl cyanoacrylate, 2-ethyl cyanoacrylate, 2-propyl cyanoacrylate, 2-butyl cyanoacrylate, 2-octyl cyanoacrylate, allyl cyanoacrylate, beta-methoxyethyl cyanoacrylate and combination thereof. A particularly desirable cyanoacrylate monomer for use herein is 2-ethyl cyanoacrylate (col. 3, lines 54-66).
A number of photoinitiators are employed by WOJCIAK
Such materials include, but are not limited to, photoinitiators available commercially from Ciba-Geigy Corp.,under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369(2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) and "DAROCUR" 1173 (2-hydroxy-2-methyl-1phenyl-1-propane) and 4265 (the combination of 2,4,6trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy 2-methyl-1-phenyl-propan-1-one); photoinitiators vailable commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn. under the "CYRACURE". The

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

list of photoinitiators, which clearly overlaps with the instantly claimed photoinitiators, is presented in col. 4, lines 41-67, col.5, lines 1-24.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one, free-radical polymerization is also known to occur in this regard under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, however, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive formulations to extend their shelf life. Thus Example 1, col. 10, 11 teaches the following:

A photocurable composition in accordance with the present invention was prepared from about 95.9 grams of 2-ethyl cyanoacrylate, about 0.1 grams of ferrocene and about 4 grams of "DAROCUR" 1173 as a photoinitiator. Typically, commercially available cyanoacrylate-containing compositions (such as "PRISM" Adhesive 4061, commercially available from Loctite Corporation, Rocky Hill, Conn.) are stabilized against free-radical formation by the addition of an acidic material, such as boron trifluoride or methane sulfonic acid. In this example, therefore, the ethyl cyanoacrylate contained about 20 ppm of boron trifluoride as an acid anionic stabilizer.

Although not all the groups of photoinitiators are disclosed by WOJCIAK, he motivates one skilled in the art to utilize stabilizers, comprising complexes of boron tetrafluoride and stabilizers against free radical formation as instantly claimed.

Claims 112 meet the criteria set out in PCT Article 33(4) for industrial applicability , the compositions as claimed are used as cyanoacrylate adhesives.

---------- NEW CITATIONS ----------
NONE

The demand must be filed directly with the competent International Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:
IPEA/ US

PCT

CHAPTER II

DEMAND

Under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of International preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA	Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION

Applicant's or agent's file reference: **ICC-211/PCT**

International application No.	International filing date *(day/month/year)*	(Earliest) Priority date *(day/month/year)*
PCT/US00/24620	**08 SEPTEMBER 2000 (08.09.00)**	**09 SEPTEMBER 1999 (09.09.99)**

Title of invention: **RADIATION-CURABLE, CYANOACRYLATE-CONTAINING COMPOSITIONS**

Box No. II APPLICANT(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

LOCTITE CORPORATION
1001 Trout Brook Crossing
Rocky Hill, Connecticut 06067
US

Telephone No.: **860.571.5000**
Facsimile No.: **860.571.5465**
Teleprinter No.:

State *(that is, country)* of nationality: **US**
State *(that is, country)* of residence: **US**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

MISIAK, Hanns R.
22 Cypress Avenue/Scholarstown Road
24 Dublin
IRELAND

State *(that is, country)* of nationality: **DE**
State *(that is, country)* of residence: **IE**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:
State *(that is, country)* of residence:

☐ Further applicants are indicated on a continuation sheet.

Form PCT/IPEA/401 (first sheet) (July 1998; reprint July 1999)

See Notes to the demand form

International application No.
PCT/US00/24620

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is [X] Agent [ ] common representative

and [X] has been appointed earlier and represents the applicant(s) also for international preliminary examination.

[ ] is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

[ ] is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

BAUMAN, Steven C.
LOCTITE CORPORATION
1001 Trout Brook Crossing
Rocky Hill, Connecticut 06067
US

Telephone No.: 860.571-5001
Facsimile No.: 860.571.5028
Teleprinter No.:

[ ] **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IIV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:*

1. The applicant wishes the international preliminary examination **to start on the basis of:**

[X] the international application as originally filed

the description [X] as originally filed
[ ] as amended under Article 34

the claims [X] as originally filed
[ ] as amended under Article 19 (together with any accompanying statement)
[ ] as amended under Article 34

the drawings [X] as originally filed
[ ] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered reversed.

3. [ ] The applicant wishes the start of the international preliminary examination **to be postponed** until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: .....English.....

[X] which is the language in which the international application was filed.
[ ] which is the language of a translation furnished for the purposes of international search.
[ ] which is the language of publication of the international application.
[ ] which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

The applicant hereby **elects all eligible States** *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes **not to elect:**

International application No.
PCT/US00/24620

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

			For International Preliminary Examining Authority use only	
			received	not received
1.	translation of international application	: sheets	☐	☐
2.	amendments under Article 34	: sheets	☐	☐
3.	copy (or, where required, translation) of amendments under Article 19	: sheets	☐	☐
4.	copy (or, where required, translation) of statement under Article 19	: sheets	☐	☐
5.	letter	: sheets	☐	☐
6.	other *(specify)*	: sheets	☐	☐

The demand is also accompanied by the item(s) marked below:

1. [X] fee calculation sheet
2. [ ] separate signed power of attorney
3. [ ] copy of general power of attorney; reference number, if any:
4. [ ] statement explaining lack of signature
5. [ ] nucleotide and or amino acid sequence listing in computer readable form
6. [X] other *(specify)*: RETURN RECEIPT POSTCARD

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

BAUMAN, Steven C., Agent
(Registration No. 33,832)

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. [ ] The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. [ ] The applicant has been informed accordingly.
4. [ ] The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. [ ] Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PCT

CHAPTER II

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No.	PCT/US00/24620
Applicant's or agent's file reference	ICC-211 PCT

For International Preliminary Examining Authority use only

Date stamp of the IPEA

Applicant

LOCTITE CORPORATION
MISIAK, Hanns, R.

Calculation of prescribed fees

1. Preliminary examination fee	490.00	P
2. Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)*	137.00	H
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	627.00	TOTAL

Mode of Payment

- [X] authorization to charge deposit account with the IPEA (see below)
- [ ] Cheque
- [ ] postal money order
- [ ] bank draft
- [ ] Cash
- [ ] Revenue stamps
- [ ] Coupons
- [ ] Other *(specify)*:

Deposit Account Authorization *(this mode of payment may not be available at all IPEAs)*

The IPEA/ US [X] is hereby authorized to charge the total fees indicated above to my deposit account.

[X] *(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

12-2135	28 March 2001	Steven C. Bauman
Deposit Account Number	Date *(day/month/year)*	Signature

Form PCT/IPEA/401 (Annex) (January 1996; reprint January 1998)

See Notes to the fee calculation sheet

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PCT

CHAPTER II

FEE CALCULATION SHEET

COPY

Annex to the Demand for international preliminary examination

International application No.	PCT/US00/24620
Applicant's or agent's file reference	ICC-211 PCT

For International Preliminary Examining Authority use only

Date stamp of the IPEA

Applicant

LOCTITE CORPORATION
MISIAK, Hanns, R.

Calculation of prescribed fees

1.	Preliminary examination fee	490.00	P
2.	Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)*	137.00	H
3.	Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	627.00	TOTAL

Mode of Payment

- [X] authorization to charge deposit account with the IPEA (see below)
- [ ] Cheque
- [ ] postal money order
- [ ] bank draft
- [ ] Cash
- [ ] Revenue stamps
- [ ] Coupons
- [ ] Other *(specify):*

Deposit Account Authorization *(this mode of payment may not be available at all IPEAs)*

The IPEA/ US [X] is hereby authorized to charge the total fees indicated above to my deposit account.

[X] *(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

12-2135	28 March 2001	Steven C. Bauman
Deposit Account Number	Date *(day/month/year)*	Signature

Form PCT/IPEA/401 (Annex) (January 1996; reprint January 1998)

See Notes to the fee calculation sheet

\\LCHQMAIN\APPS\User\BaumanS\WORD\PATENTS\PCT DEMAND FEE CALC\ICC-211.doc

COPY

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL CT 06067

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference ICC-211/PCT	Date of Mailing *(day/month/year)* 02 JAN 2001 **FOR FURTHER ACTION** **See paragraphs 1 and 4 below**
International application No. PCT/US00/24620	International filing date *(day/month/year)* 08 SEPTEMBER 2000
Applicant LOCTITE CORPORATION	

1. [X] The applicant is hereby notified that the international search report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 *bis* 1 and 90 *bis* 3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-8819

(See notes on accompanying sheet)

Form PCT/ISA/220 (July 1998)★

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL CT 06067

RECEIVED
JAN - 4 2001
IP DEPARTMENT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

Date of Mailing *(day/month/year)*	02 JAN 2001
Applicant's or agent's file reference ICC-211/PCT	**FOR FURTHER ACTION** **See paragraphs 1 and 4 below**
International application No. PCT/US00/24620	International filing date *(day/month/year)* 08 SEPTEMBER 2000
Applicant LOCTITE CORPORATION	

1. [X] The applicant is hereby notified that the international search report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 *bis* 1 and 90 *bis* 3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-8819

(See notes on accompanying sheet)

Form PCT/ISA/220 (July 1998)*

PATENT COOPERATION TREAT

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference ICC-211/PCT	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US00/24620	International filing date *(day/month/year)* 08 SEPTEMBER 2000	(Earliest) Priority Date *(day/month/year)* 09 SEPTEMBER 1999
Applicant LOCTITE CORPORATION		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (See Box II).

4. With regard to the **title,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ____

[ ] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24620

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08F 2/50, 236/12, 2/50, 4/42; CO9D 3/80; C08J 7/04, 4/04
US CL : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0; STN CA PLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,139,388 A [REICH et al] 13 February 1979, abstract, col.2, lines 47-57, Example 1, claims 1,2.	1-4, 12/5-9, 14-18 --- 1-4, 12/5-9, 14-18
Y	US 5,922,783 A [WOJCIAK] 13 July 1999, abstract, col.3, lines 14-21, 54-64, col.4, lines 41-67, col.5, lines 1-24, 42-45, 53-60, col.6, lines 2220-34, 42-50, col.7, 43-53, Example 1.	1-19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 11 OCTOBER 2000	Date of mailing of the international search report 02 JAN 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-8819

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24620

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,530,037 A [MCDONELL et al] 25 June 1996, abstract, col.3, lines 60-66, col.4, 5, col.7, lines 14-16, Example 1, claims 1-3, 7, 11, 16, 17.	1-5, 7, 12, 14-18/6, 8-11, 13, 19 ---------- 1-5, 7, 12, 14-18/6, 8-11, 13, 19
A	EP 0 274 595 A (GENERAL ELECTRIC COMPANY) 20 July 1988, entire document.	1-19
A --- Y	US 3,940,362 A [OVERHULTS] 24 February 1976, abstract, col.2, lines 42-45, col.3, lines 15-18, 44-50, col.4, lines 55-60, col.5, lines 10-20, Examples I-XXVI, claims 1-9, 19, 21.	1-19 ----- 1-19
A	US 5,824,180 A [MIKUNI et al] 20 October 1998, entire document	1-19
A --- Y	EP 0 769 721 A (THREE BOND CO., LTD) 23 April 1997, abstract, page 3, page 10, 19-59, page 11, lines 1-5, 40-46, page 12, Table 1.	1-19 ------ 1-19

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty and of the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule" and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended ?

The claims only.

The description and the drawings may only be amended during international preliminary examination under Chapter II.

When ? Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments ?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How ? Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

What documents must/may accompany the amendments ?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confounded with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

(i) the claim is unchanged;
(ii) the claim is cancelled;
(iii) the claim is new;
(iv) the claim replaces one or more claims as filed;
(v) the claim is the result of the division of a claim as filed.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL CT 06067

PJP
11/28/01

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference ICC-211/PCT	Date of Mailing *(day/month/year)* 21 NOV 2001
	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority Date *(day/month/year)*
PCT/US00/24620	08 SEPTEMBER 2000	09 SEPTEMBER 1999

Applicant
LOCTITE CORPORATION

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

rm PCT/IPEA/416 (July 1992)★

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL CT 06067

PCT

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference ICC-211/PCT	Date of Mailing *(day/month/year)* 21 NOV 2001
	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority Date *(day/month/year)*
PCT/US00/24620	08 SEPTEMBER 2000	09 SEPTEMBER 1999

Applicant
LOCTITE CORPORATION

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

Form PCT/IPEA/416 (July 1992)★

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference ICC-211/PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/24620	International filing date *(day/month/year)* 08 SEPTEMBER 2000	Priority date *(day/month/year)* 09 SEPTEMBER 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant LOCTITE CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   I [X] Basis of the report

   II [ ] Priority

   III [ ] Non-establishment of report with regard to novelty, inventive step or industrial applicability

   IV [ ] Lack of unity of invention

   V [X] Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI [ ] Certain documents cited

   VII [ ] Certain defects in the international application

   VIII [ ] Certain observations on the international application

Date of submission of the demand 30 MARCH 2001	Date of completion of this report 18 OCTOBER 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TANYA ZALUKAEVA DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-0651

Form PCT/IPEA/409 (cover sheet) (July 1998)*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/24620

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed

☒ the description:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

☒ the claims:
pages (See Attached), as originally filed
pages _____, as amended (together with any statement) under Article 19
pages _____, filed with the demand
pages _____, filed with the letter of _____

☒ the drawings:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

☒ the sequence listing part of the description:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. 8

☒ the drawings, sheets/~~fig~~ NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

*** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/24620

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	5-7,9, 10-20	YES
	Claims	1-4, 12	NO
Inventive Step (IS)	Claims	NONE	YES
	Claims	1-7, 9-19	NO
Industrial Applicability (IA)	Claims	1-7, 9-19	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-7, 9-19 lack an inventive step under PCT Article 33(3) as obvous over McDONNELL et al (U.S. 5,530,037)

McDONNELL discloses a curable cyanoacrylate adhesive composition intended for medical and/or veterinary uses is sterilized in liquid form by gamma irradiation. The composition comprises

a) a cyanoacrylate monomer

b) a combination of an anionic stabilizer and a free-radical stabilizer in amounts effective to stabilize the composition during irradiation and to stabilize the sterilized composition during storage prior to cure, wherein the free radical stabilizer is a selected phenolic antioxidant (abstract, col.3, lines 60-66). Phenolic antioxidant is presented by compounds of formula (I), (col. 4, lines 1-5), which depicts a p-benzoquinone.

The cyanoacrylate monomer may be selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl,tert-butyl, n-pentyl, iso-pentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, allyl, methoxyethyl,ethoxyethyl, 3-methoxybutyl and methoxyisopropyl cyanoacrylate esters (col. 4, lines 61-67).

One of preferred antioxidants is butyl hydroxy toluene (BHT, or 4-methyl-2,6-di-tert-butylphenol

Other anti-oxidants which may be used include methyl hydroquinone, catechol, tert-butyl hydroquinone, 4-tert-butoxyphenol, 4-ethoxyphenol, 3-methoxyphenol, 2-tert-butyl-4-methoxyphenol, and 2,2-methylene-bis-(4-methyl-6-tert-butylphenol).

Anionic (acid) stabilizers for cyanoacrylate adhesives include Sulphur Dioxide, Sulphonic Acids, Sulphuric Acid, Sulphur Trioxide, Phosphorous Acids, Carboxylic Acids, Picric Acid, Boron Trifluoride, etc. (col. 5, lines 35-66, col. 6, lines 1-5.

In specific regard toclaims 6, 8-11

McDONNELL discloses a cyanoacrylate adhesives as instantly (Continued on Supplemental Sheet.)

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

CLASSIFICATION:
The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): C08F 2/50, 236/12, 2/50, 4/42; C09J 7/04 and US Cl.: 526/172, 298, 170, 171; 522/18, 19, 20, 25,28, 29, 173.

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,
page(s) 1, 2, 5-10, 12-20, 22-27, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
3, 4, 11, 21, filed with the letter of 13 August 2001

This report has been drawn on the basis of the claims,
page(s) NONE, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) NONE, filed with the demand.
and additional amendments:
28-31, filed with the letter 13 August 2001

This report has been drawn on the basis of the drawings,
page(s) NONE, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
claimed, however does not disclose the same photoinitiators, as per instant claims 6, 8-11. Because the polymerization of MCDONNEL takes place under gamma-irradiation, one skilled in the art would have found it obvious to introduce imitators capable of producing radicals under irradiation with very short wavelength, which are mostly the instantly claimed compounds, and thus to arrive at the instant claims.

Claims 1-7, 9 lack an inventive step under PCT Article 33(3) as being obvious over WOJCIAK (U.S. 5,922,783).
WOJCIAK discloses radiation-curable composition which includes a cyanoacrylate component or a cyanoacrylate-containing formulation, a metallocene component and a polymerizingly effective amount of a photoinitiator to accelerate the rate of cure (abstract).

The cyanoacrylate monomer is selected from methyl cyanoacrylate, 2-ethyl cyanoacrylate, 2-propyl cyanoacrylate, 2-butyl cyanoacrylate, 2-octyl cyanoacrylate, allyl cyanoacrylate, beta-methoxyethyl cyanoacrylate and combination thereof. A particularly desirable cyanoacrylate monomer for use herein is 2-ethyl cyanoacrylate (col. 3, lines 54-66).
A number of photoinitiators are employed by WOJCIAK
Such materials include, but are not limited to, photoinitiators available commercially from Ciba-Geigy Corp.,under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369(2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) and "DAROCUR" 1173 (2-hydroxy-2-methyl-1phenyl-1-propane) and 4265 (the combination of 2,4,6trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy 2-methyl-1-phenyl-propan-1-one); photoinitiators vailable commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn. under the "CYRACURE". The

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

list of photoinitiators, which clearly overlaps with the instantly claimed photoinitiators, is presented in col. 4, lines 41-67, col.5, lines 1-24.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one, free-radical polymerization is also known to occur in this regard under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, however, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive formulations to extend their shelf life. Thus Example 1, col. 10, 11 teaches the following:

A photocurable composition in accordance with the present invention was prepared from about 95.9 grams of 2-ethyl cyanoacrylate, about 0.1 grams of ferrocene and about 4 grams of "DAROCUR" 1173 as a photoinitiator. Typically, commercially available cyanoacrylate-containing compositions (such as "PRISM" Adhesive 4061, commercially available from Loctite Corporation, Rocky Hill, Conn.) are stabilized against free-radical formation by the addition of an acidic material, such as boron trifluoride or methane sulfonic acid. In this example, therefore, the ethyl cyanoacrylate contained about 20 ppm of boron trifluoride as an acid anionic stabilizer.

Although not all the groups of photoinitiators are disclosed by WOJCIAK, he motivates one skilled in the art to utilize stabilizers, comprising complexes of boron tetrafluoride and stabilizers against free radical formation as instantly claimed.

Claims 112 meet the criteria set out in PCT Article 33(4) for industrial applicability , the compositions as claimed are used as cyanoacrylate adhesives.

Response to Arguments

Applicants' arguments were fully considred, but they are not persuasive. Since the reference to REICH was removed from the scope of rejection, Examiner does not address the arguments on this reference. In regard to McDONALD reference the very first word of the abstarct cites "curable adhesive compositions comprising cyanoacrylate monomer, combination of stabilizers including a compound capable of generating free radicals

As for Applicant's arguments about the intended use of the instant composition compare to that of McDonald, it is well set that a new use of otherwise known or obvious composition does not impact its patentability.

In regard to WOJCIAK reference, which in fact uses the mixture of a metallocene and a free radical component, Examiner notices, that first of all the transitional word "comprising",as per instant claim 1 leaves the possibility of the presence of any other components, even in the major amounts. Secondly, the rejection was made as an obviousness rejection, not as anticipation one, and as shown above reference itself suggests to one skilled in the art the particularities of the instantly claimed composition.

---------- NEW CITATIONS ----------

NONE

includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters, examples of which are expressed as 2-cyanoethyl acrylate (CH_2=CHCOOCH_2CH_2CN) and 3-cyanopropyl acrylate (CH_2=CHCOOCH_2CH_2CH_2CN). (See page 5, lines 19-26.)

U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

In C. Kutal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^-, cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Kutal) 5,691,113 (Kutal) and 5,877,230 (Kutal).

International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α-cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VIII of the periodic table and aromatic electron system ligands selected from π-arenes, indenyl, and η-cyclopentadienyl. The photocurable composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni) describes such compositions in the context of a method of bonding artificial nails.

describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional

applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a photoinitiated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α-halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phospine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinititor component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of

What Is Claimed Is:

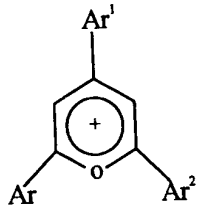
1. A photocurable composition comprising:

(a) a 2-cyanoacrylate component,

(b) a photoinitiated radical generating component, and

(c) a photoinitiator component,

wherein the photoinitator component is selected from the compounds within the following structure:



wherein each of Ar, Ar^1 and Ar^2 are aryl groups, with or without substitution, and X^- is an anion.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by $H_2C=C(CN)-COOR$, wherein R is selected from the group consisting of C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α-haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclohexane, 2,5-bis(t-butylperoxy)-2,4-

7. (Amended) The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-trimethyl pentyl phosphine oxide, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to Claim 1, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to Claim 1, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to Claim 1; and

(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to Claim 1 in a two-part formulation.

17. The composition according to Claim 1 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to Claim 1 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to Claim 1, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.